THE

LONDON, EDINBURGH, ᴀɴᴅ DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

———◆———

[SIXTH SERIES.]

AUGUST 1923.

XXIV. *The Electrification produced by the Pulverization of Aqueous Solutions.* By Prof. J. J. NOLAN, *M.A., D.Sc., and* Rev. H. V. GILL, *S.J., M.A., M.Sc., University College, Dublin*[*].

IN a previous paper[†] one of the present writers and another have examined the electric charges produced when water of different degrees of purity is broken up in contact with the air. It was found that the purity of the water was specially important when the degree of breaking-up was small, the purer water yielding the higher charges. When the water was broken into very fine drops, this difference tended to disappear, and it seemed possible that if a sufficient degree of pulverization could be attained, all samples of water would give identical charges. It was also found that as the purity increased, the water was more easily broken into small drops. Considered in connexion with Simpson's theory of thunderstorm electricity, the magnitudes of charge observed showed that if a moderate degree of purity were attributed to the rain-drops in a thunderstorm, the breaking of the drops in the manner supposed by Simpson would produce sufficient separation of electricity to account for the observed effects.

In the work referred to, the purity of the water was varied

---

* Communicated by the Authors.

† J. J. Nolan and J. Enright, Sci. Proc. Roy. Dublin Soc. xviii. p. 1 (1922).

Phil. Mag. S. 6. Vol. 46. No. 272. *Aug.* 1923.   Q

by mixing distilled water with tap-water in various proportions. It is important to put the matter on a more definite footing, and to ascertain to what extent the charge is affected by the substances ordinarily present in rain, in the concentrations at which they usually occur. We shall then be in a better position to form an opinion as to how far the results on distilled water are applicable to the breaking up of rain-drops in the atmosphere. The investigation of this point had led to a wider investigation of the effect of dissolved substances in general. Another obvious extension of the work is the examination of water of a still higher degree of purity. The distilled water available for this and the previous work had a specific conductivity as high as $2 \cdot 4 \times 10^{-6}$ ohm^{-1}. As water of conductivity $\cdot 1$ to $\cdot 2 \times 10^{-6}$ can be prepared without much difficulty, it is clear that there is a considerable range available for investigation. Work on the latter point is now proceeding ; the present paper deals with the effect of the ordinary impurities in rain, and then with the effect of dissolved substances in general.

General Experimental Method.

Experiments on the electric charges produced by breaking up water solutions have been carried out by many observers, especially by Lenard[*], Sir J. J. Thomson[†], J. J. Rey[‡], and Christiansen[§]. In almost all cases the breaking up of the liquid was produced by allowing drops to splash against an obstacle. It is not to be expected perhaps that the spraying method used by us should give the same results as the method of splashing, although previous work[‖] has shown that, in the case of pure water at least, the charge on the water, considered as a function of the new area of surface produced, was the same whether the water was sprayed or broken by falling into an air stream. But, in fact, our results for solutions exhibit considerable differences from those obtained by the splashing method. The method of spraying has the advantage that the degree of breaking up of the liquid is easily controlled and measured. The breaking up can also be carried to a far higher degree, if necessary, than is possible with the other method.

[*] P. Lenard, Wied. *Ann.* xlvi. p. 584 (1892).

[†] J. J. Thomson, Phil. Mag. xxxvii. p. 341 (1894).

[‡] J. J. Rey, *L'ionisation de l'air par les chutes d'eau.* Gauthier-Villars, 1912.

[§] Christiansen, *Ann. der Physik,* xl. pp. 107, 233 (1913), clix. pp. 95, 280 (1919).

[‖] J. J. Nolan, Proc. Roy. Soc. A. xc. (1914).

The method of working is given in some detail in the previous paper[*]. The liquid is sprayed in a horizontal direction from a metal sprayer driven by air under pressure. The drops fall into an insulated metal tray. This, together with the sprayer itself, which is also insulated, is connected to a Dolezalek electrometer which measures the charge. The electrometer therefore records the charge on the water due to the electric separation at the water-air surface, the charge of the opposite sign being carried off in the air as an excess of ions of one sign. The method of measuring the size of the drops corresponding to each pressure on the sprayer and of computing the corresponding new area of liquid surface produced need not be repeated here.

Part I.

Effect of Substances occurring in Rain.

In examining solutions of different substances there are two lines of procedure open to us : we can keep the concentration of the solution constant and examine the charge corresponding to different degrees of pulverization, or we can drive the sprayer at a steady pressure and examine the effect of solutions of different strengths. The latter is the method of most interest, especially in the present case. The degree of breaking-up likely to be experienced by raindrops in nature is even smaller than the smallest produced by our sprayer. Hence we can best examine the effect of the different possible impurities by working at a steady low pressure of the sprayer.

The substances most likely to be present in rain in the free atmosphere are nitrates and nitrites, sodium chloride from evaporated sea spray, hydrogen peroxide and dissolved gases such as ammonia, carbon dioxide, oxygen, and nitrogen. It may be stated at once that, judging from their effect when added to distilled water, these substances, with the single exception of sodium chloride, will not seriously affect the charge developed when a rain-drop is broken. In illustration of this we quote the results obtained when solutions of nitric acid, ammonia, and sodium chloride of various strengths are sprayed. In each case the solutions were sprayed into drops of an average radius of 7.5×10^{-3} cm. The charges per c.c., which are all positive, are given in arbitrary units, the value for distilled water being taken as 100.

* J. J. Nolan and J. Enright, *loc. cit.*

Standard solution of HNO_3 ......   94·5 milligrams per litre.
,,   ,,   ,, NH_3 ......   15·4   ,,   ,,   ,,
,,   ,,   ,,   NaCl ......   40·0   ,,   ,,   ,,

Positive charge—Distilled water 100.

Strength of Solution.				HNO_3.	NH_3.	NaCl.
2 per cent. of standard				82	89	95
5	,,	,,	,, ...	53	83	86
10	,,	,,	,, ...	22	74	66
20	,,	,,	,, ...	14	57	57
30	,,	,,	,, ...	...	47	47
50	,,	,,	,, ...	10	45	38
100	,,	,,	,, ...	7	42	23

The amount of ammonia present in rain collected in country districts may be taken as about ·5 mg. per litre. In the tropics the value seems to be higher[*]. Similarly for nitric acid, while the values for the tropics are of the order of ·2 mg. per litre[†], the values found by Boussingault in Alsace and the values found at Rothamsted range from ·2 to ·4 mg. per litre. Taking the value ·5 mg. for ammonia and ·3 mg. for nitric acid, we find that these concentrations correspond to about $\frac{1}{3}$ per cent. of our standard solution in each case. The observations show that ammonia and nitric acid in such quantities would produce no appreciable effect on the charge produced by breaking drops. Even in the concentrations reported from the tropics, these substances, while producing a noticeable effect, would not seriously interfere with the phenomenon. It is otherwise however in the case of sodium chloride. The concentration of this substance in rain varies very widely, depending upon the distance from the sea-shore. McAdie[‡] quotes the following values: England (mean) 2·2 mg. per litre. Rothamsted 2·01 mg., Nantes 14 mg., and Troy, New York, 2·7 mg. It would appear that in places remote from the sea shore the concentration can sink below 1 mg. per litre. This would correspond roughly to 2 per cent. of our standard solution of NaCl, and, as will be seen, the corresponding reduction in the charge on the water is only 5 per cent. The mean concentration for England would produce a reduction of nearly 20 per cent. in the values for distilled water, while the figure quoted for Nantes, which is no doubt exceeded at many sea-coast stations, would reduce the charging to

* Marcato & Muntz, *C. R.* cxiv. p. 184 (1892).
† Marcato & Muntz, *C. R.* cviii. p. 1062 (1889).
‡ McAdie, 'Principles of Aerography,' p. 164. Harrap, 1917.

45 per cent. of the value found with pure water. It is clear then, that in many cases the NaCl content of the rain-water is important, and that while in inland regions the charge developed when a rain-drop is broken will have very nearly the full value, in sea-coast regions this may be reduced to a half or a third.

Effect of Nitrites, H_2O_2, and Atmospheric Gases.

The conclusions reached for nitric acid and ammonia hold for the remaining substances. Nitrites and carbon dioxide in the concentrations in which they occur in rain do not seriously affect the charge given by distilled water. We have also tested air-free water and water saturated with air against ordinary distilled water. We were unable to find any consistent difference. Hydrogen peroxide in the quantity in which it occurs in rain (up to 1 mg. per litre*) does not produce any noticeable effect.

Inhibition of Thunderstorms.

While it is clear that sodium chloride is the only substance occurring naturally in rain that is likely to seriously diminish the charge produced by a breaking drop, it is of interest to inquire what concentrations of some other substances would be required to produce this effect. Some experiments made with ammonia showed that the charging was reduced to 1 per cent. of the value for pure water with a solution containing about ·5 gramme NH_3 per litre. If Simpson's theory of thunderstorms is correct, it would seem that if ammonia could be introduced into the thunder-cloud in sufficient quantity to form with the rain-drops a solution of this strength (or even $\frac{1}{10}$ of this strength) the development of a thunderstorm would be seriously impeded. This is an experiment which is perhaps within the bounds of possibility.

It would also appear that in view of the unusual quantities of inorganic matter in the air over large industrial centres, the frequency and severity of thunderstorms should be somewhat less in these regions. We are not in the possession of any records by which this possibility could be tested.

Tests on Rain-Water.

The inquiry which we are carrying out could be made in another fashion—that is, by making the actual tests on rain-water. The rain-water should be collected in districts

* Schöne, *Berichte*, 1878, p. 482.

remote from towns, in order that the risk of artificial con-
tamination should be as low as possible. The manner of
collection and transport should be devised so as to preserve
the water as closely as possible in its natural state. We
have endeavoured to secure some samples in this way, but
the conditions prevailing recently in the districts most suit-
able for the collection of pure rain-water have not been
favourable. Some results may, however, be quoted. A
sample collected in Dublin and visibly contaminated with
soot gave 35 per cent. of the effect of distilled water. A
sample collected near Carnsore Point, co. Wexford (28th Feb.,
1923, wind S.W.), gave 40 per cent. of the effect of distilled
water. This sample probably contained a good deal of
sodium chloride.

We hope to continue these tests at a later date. But even
without the extra information which they would yield, our
conclusions are fairly clear. Except in the neighbourhood
of the sea, the rain-drops may be expected to give nearly the
same electrical effects as the distilled water of our experi-
ments. The conclusions of the former paper may therefore
be reaffirmed. It was there shown that a rain-drop of
diameter 4 mm. breaking in a natural fashion would acquire
a positive charge somewhat greater than ·2 electrostatic
unit per c.c. Taking into consideration the tendency for
evaporation to further concentrate the charge, we consider
that the breaking of the drops in the manner supposed by
Simpson can yield sufficient electric charge to account for
the observed phenomena of the thunderstorm.

Part II.

Investigation of the Effect in general.

Inorganic Salts—Sodium Chloride.

While this research was intended originally as an investi-
gation into the physical basis of Simpson's theory, it was
soon found desirable to extend its scope. We had noticed
that all inorganic substances which we tested behaved in
very much the same way. With increasing concentration
they gradually diminished, but did not (within the limits of
concentration used by us) reverse or annul the positive charge
due to pure water. We wished to observe the behaviour of
a substance which would produce a reversal of sign. If there
is anything which has been regarded as well established
about electrification by the breaking of water, it is that sodium
chloride in increasing quantities first diminishes and then

reverses the positive charge obtained with pure water. This result was found by Lenard[*] in his pioneer work on the subject. He found that the solution began to give a negative charge at a concentration of less than ·01 per cent. NaCl, and that the maximum negative charge was given by a solution of 6·5 per cent. J. J. Rey[†] found that the charge changed sign at a concentration of about ½ gramme of NaCl per litre, and that it reached a maximum negative value at about 10 grammes per litre.

In an extended series of tests made by our method, using solutions of strengths varying from 100 grammes NaCl per litre down to the very dilute solutions mentioned in the first part of this paper, we were unable to detect any indication of negative charging. This was the case not only with sodium chloride but with all inorganic salts which we tested. For example, chromium trioxide and potassium permanganate, which at concentrations of ·0064 and ·25 grammes per litre respectively gave negative charges in Sir J. J. Thomson's work, were with us always positive. In all cases increasing concentration diminished the positive effect due to pure water, but in no case were we able to obtain a reversal of sign. We did not test all the salts mentioned by other writers, as in order to clear up the discrepancy, we thought it best to confine our attention to the outstanding case of sodium chloride.

It was natural to infer that the real difference between the spraying and the splashing methods was a difference in the degree of pulverization produced. The sprayer breaks up the water very effectively, and the charges produced are very much higher than those obtained on water which has splashed. We might assume then, that the failure to obtain negative charging with salt solutions was in some way due to a too drastic pulverization of the liquid. The negative charge might be expected to appear if the pulverization were reduced to something corresponding to that produced by splashing. The extent to which the liquid is broken up can be controlled by varying the air-pressure at which the sprayer is driven. This necessitates the consideration at this stage of the relation between these two quantities, air-pressure and pulverization.

This point has not arisen before in this paper, as up to the present we have been comparing different solutions which were all sprayed at the same pressure and broken into drops

[*] Lenard, *loc. cit.*
[†] Rey, *loc. cit.*

of the same size.   The graphs of fig. 1 (which is in the main taken from a previous paper[*]) show the efficiency of the sprayer at different pressures.   The area of liquid surface per c.c. of water sprayed (or what is roughly the same thing $\frac{3}{r}$, r being the mean radius of the drops) is plotted against the pressure on the sprayer.   The lower set of graphs deal with distilled water, tap-water, and a mixture of the two.

Fig. 1.
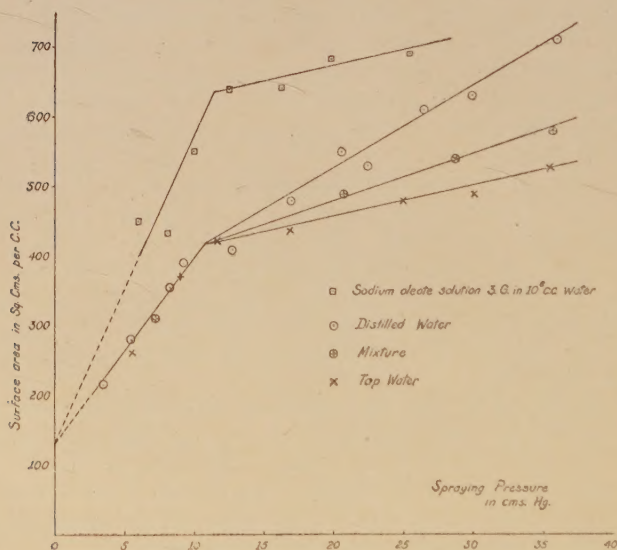
It is clear that the three samples of water behave as one until a pressure of 11 cm. Hg is reached.   Then they separate, and the pure water is, at a given pressure, broken into smaller drops than the less pure samples.   We have not gone through the rather laborious process of taking observations on the sizes of drops at various pressures for any of the sodium chloride solutions.   We have assumed that the dilute solutions would not differ very much in their behaviour, at pressures below 11 cm. Hg, from the three water samples.

If, as already suggested, the non-appearance of the negative charge for salt solutions is due to excessive pulverization, we

[*] Nolan & Enright, *loc. cit.*   In the graphs given in the previous paper some points were accidentally omitted by the draughtsman.   They have been restored here.

might expect to detect the change of sign by working from
10 cm. Hg (the normal spraying pressure) downwards.
We have therefore on many occasions tested salt solutions
at every available spraying pressure. At the lowest pressure
at which the sprayer would function we obtained no indica-
tion of negative charge. Solutions of a strength which
according to Lenard and Rey should have been definitely
negative were with us definitely positive, the positive charge
increasing with increasing pressure on the sprayer.

It was not until after the completion of most of the work
described subsequently in this paper, that we finally obtained
a negative charge from salt solutions. The result was ulti-
mately arrived at (contrary to our expectations) by testing
strong solutions at *high* degrees of pulverization. We give
some results obtained for a solution of 30 grammes NaCl per
litre and also for sea-water. The values for the latter are
the means of observations on three samples collected at
Howth, Blackrock, and Dalkey.

	PRESSURE.			
	10 cm.	20 cm.	30 cm.	40 cm.
NaCl solution 30 g./litre	+14	+4	−32	−76
Sea-water	+23	+9	−26	−70

The numbers given represent in arbitary units the charge
produced per second. In order to compare them with one
another, one must not only take account of the differing
degrees of pulverization, but of the increasing quantity of
water driven through the sprayer at the higher pressures.
It is enough, however, at present to see that the negative
charge has made its appearance at the high degrees of
pulverization. In order to give an idea of relative magni-
tudes of charge, it may be stated that on the scale of the
figures quoted, the charging of distilled water at 10 cm.
pressure would be represented by about 2000, and at 40 cm.
pressure by about 15,000. It may also be stated that while
the three samples of sea-water yielded results in very good
agreement, solutions of NaCl of apparently uniform concen-
tration gave results which fluctuated very considerably.
The values given above represent a set of observations on
one particular day. It is of little advantage to give a mean
value of many observations, as the fluctuations were very
irregular. The further consideration of the appearance of
the negative charge in these cases can with advantage
be deferred to a later stage in this paper.

The general conclusions reached in this section may be re-stated. Inorganic salts (as far as our examination goes) diminish the positive charging due to distilled water, but do not reverse it except (in the case of NaCl, at least) when strong solutions are subjected to a high degree of pulverization. The negative charging then produced is relatively very small and irregular.

Non-Electrolytes.

We have carried out tests on a number of substances which do not dissociate in aqueous solution. These included glucose, maltose, lactose, and urea. Solutions of different strengths were examined. We could find no certain difference between these solutions and distilled water. Certain effects must be guarded against. It is clear that if the substance under test is impure, the impurity may be present in sufficient quantity in a strong solution to seriously affect the charge. A strong solution of maltose which readily frothed on being shaken up (in itself a sign of impurity) gave a charge much less than that of distilled water. This we explained in the fashion just mentioned. On the general evidence of the other substances, we concluded that non-electrolytes are ineffective in interfering with the normal charging produced when pure water is broken up.

Very Active Substances.

We have next to consider a group of substances which affect the electric charge developed by water very strongly. The effects produced by some substances of this class have been examined by Sir J. J. Thomson and others. We first noticed this effect with sodium oleate. This substance when present in water, even in very small quantities, readily reverses the charge. The curves in fig. 2 show how the charge produced depends upon the degree of concentration when the sprayer is driven at our standard pressure (10 cm. Hg). The positive charge on distilled water is reduced to zero by the addition of between 2 and 2·5 grammes of sodium oleate per 10^6 c.c. At higher concentrations the charge is negative, a maximum negative value being reached at about 20 grammes per 10^6 c.c. When relatively very high concentrations are reached the charge changes sign once more. The positive charge appears at a concentration a little less than 5 g. per litre.

To show the sharpness of the first reversal of sign, we quote the following observations :—

		Charge.
Distilled water		$+120$
1 g. Sodium oleate per 10^6 c.c. water		$+ 71.5$
2 g. ,, ,, ,, ,,		$+ 19.5$
2.5 g. ,, ,, ,, ,,		$- 16$
3 g. ,, ,, ,, ,,		$- 41.$

The activity of the sodium oleate solutions changes with time. The numbers given above refer to freshly prepared solutions. A curve is given (fig. 2) for solutions which

Fig. 2.
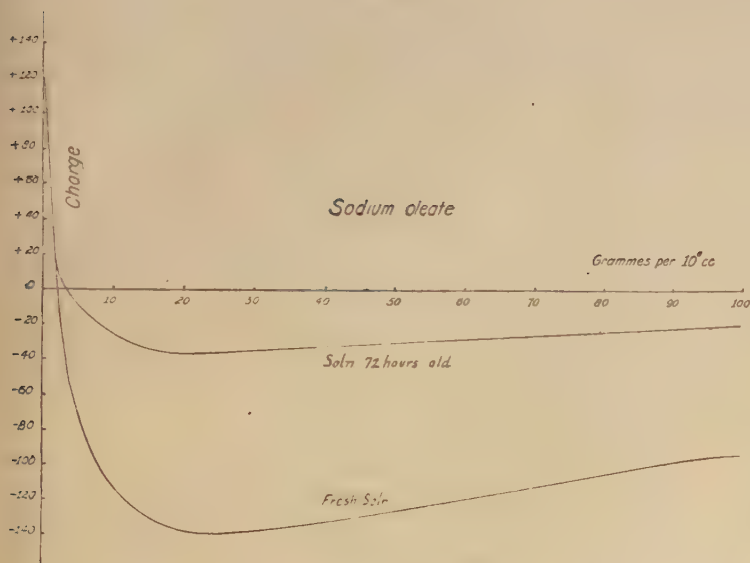
were three days old. The negative charging is much less marked. It was noticed that while the more dilute and the stronger of these solutions were quite clear, those of middle strengths showed some opacity. All solutions were quite transparent when first prepared. On testing, it was found that the more opaque solutions corresponded roughly with those giving the greater negative charges. This effect would seem to be connected with the periodic opacity of colloids investigated by Holker*.

* Holker, Proc. Roy. Soc. A. cii. p. 710 (1923).

The tests described were made with the sprayer working at the usual pressure. We also investigated the effect of varying the degree of pulverization, keeping the strength of the solution constant. The result of a test is shown in fig. 3. A solution of 3 grammes sodium oleate per 10^6 c.c. when freshly prepared gives a negative charge, the charge increasing with the degree of pulverization. When one day old it gives a small positive charge at low pressure, changing over to a weak negative at high pressure and back again to

Fig. 3.
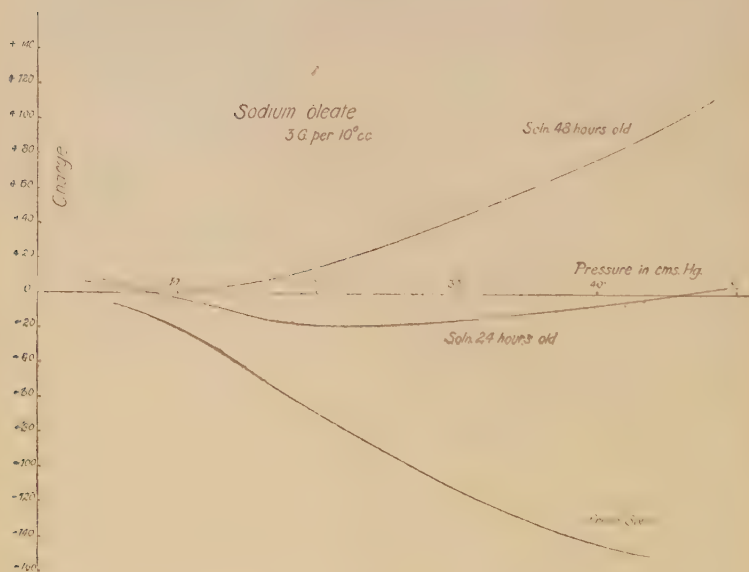
positive at still higher pressures. The solution when two days old is positive for all degrees of pulverization.

For the same solution we also investigated the relation between the pressure on the sprayer and the degree of pulverization produced. The relation is shown graphically in fig. 1. We were surprised to find that at all pressures the pulverization produced was much greater than in the case of distilled water. There is no doubt about this result, as a set of observations was made alternately with the solution and with distilled water. The values found for the latter were in good agreement with the values found previously (Nolan & Enright). Observations were made on

solutions of different ages : all gave approximately the same results*.

The pulverizing action of the sprayer changes at a pressure of about 11 cm. Hg, where all the graphs bend over. The pulverization produced in the two stages seems to depend on two different properties of the liquid. Whatever property is concerned in the first stage does not seem to be affected by the addition of tap-water to distilled water ; the three lower graphs have that part in common. The property concerned in the second stage is affected by the impurity of tap-water, and the impurity operates to reduce the pulverization. On the other hand, in the case of the sodium oleate solution, all the ordinates of the first part of the graph are increased by over 40 per cent.†. The second part is approximately parallel to the corresponding part of the graph for tap-water. Thus the sodium oleate, while modifying in the same fashion and to about the same degree as the impurities of tap-water the property of pure water involved in the second stage, operates in a novel and very marked fashion to increase the pulverization in the first stage. We are inclined to associate the effect in the first stage with the dynamic surface tension. Freundlich‡, following Lord Rayleigh§, finds for the dynamic surface tension by the jet method the value 79 dynes/cm. for solutions of sodium oleate of concentrations ·025 and ·25 per cent., while the value found for pure water is 75.

Methylene Blue, Congo Red, Methyl Orange, and Sodium Glycocholate.

Curves for methylene blue and congo red are given in fig. 4. Methylene blue produces a remarkable effect, ·5 gramme per 10^6 c.c. of water being sufficient to reduce the positive charge to zero. The negative charge has a sharp maximum at 2·5 g. per 10^6 c.c., and the charge once more becomes positive at about 11 g. per 10^6 c.c. In addition to the observations which are plotted and which were taken at our standard spraying pressure (10 cm. Hg), we

* For observations on sodium oleate and for checking the previous results on distilled water, we are much indebted to Mr. A Fynn, S.J.

† By more than 60 per cent. if we assume that the intersection of the graph with the axis gives the true zero of surface. See Nolan & Enright, *loc. cit.* p. 8.

‡ Freundlich, *Kappilarchemie*, p. 56 (1909).

§ Rayleigh, Proc. Roy. Soc. A. xlvii. p. 281 (1890).

also took observations at double that pressure. The reversal of sign now occurred at some concentrations below ·4 g. per 10^6 c.c. The maximum negative charge occurred at exactly the same concentration as before, and the second reversal took place at 13 g./10^6 c.c. instead of 11 g./10^6 c.c. All readings were much increased, the maximum negative reading being four times as great as before. With congo red the effects are not so striking. At very small concentrations there appears to be a sharp dip in the values for charge. Then follows a rise to a value slightly greater than that for pure water, and subsequently a slow falling-off.

Fig. 4.

In fig. 5 are shown the results of measurements on methyl orange. Here the effects are well defined. There is first a 33 per cent. rise from the value for water to a sharply-defined positive maximum at ·75 g./10^6 c.c. The positive charge is reversed at 5·5 g./10^6 c.c., and a negative maximum is reached in the neighbourhood of 24 g./10^6 c.c. The negative charge decreases, and the solution goes positive once more at a concentration of about ·8 g. per litre.

The behaviour of these four substances—sodium oleate, methylene blue, congo red, and methyl orange—differs in a very remarkable way from that of the ordinary inorganic salts and of non-electrolytes. In a research on adsorption,

Lewis[*] has found a group of substances which depart widely from the adsorption law founded on thermodynamic reasoning by Willard Gibbs. The expression arrived at by Gibbs is

$$\gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc},$$

where γ is the excess surface concentration of the solute, c the bulk concentration, and σ the interfacial tension. Lewis found that this law held fairly well for ordinary inorganic

Fig. 5.
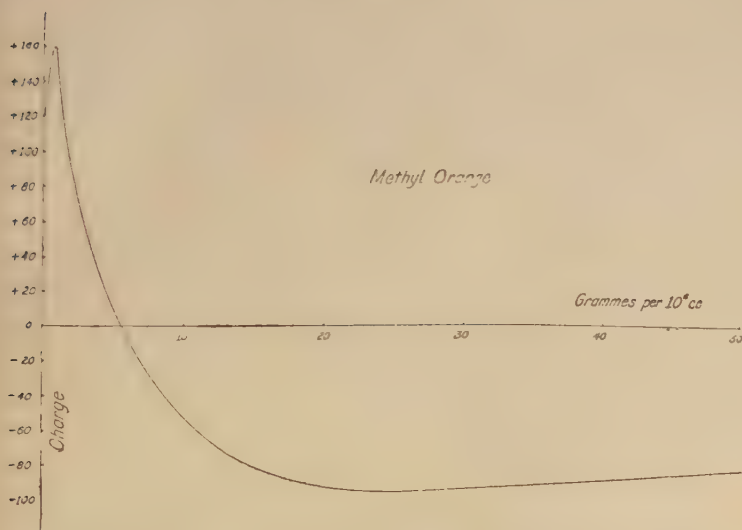
salts and for caffeine, a non-electrolyte ; but he noted very wide departures from it in the case of four substances : sodium glycocholate congo red, methyl orange, and sodium oleate. These substances appeared to be present in the surface layers in concentrations of the order 100 times as great as would be expected from the variation of surface tension with concentration, assuming that Gibbs's law holds. As three of these substances are found by us to be equally remarkable in their electric effects in very dilute solution, we decided to test the fourth. A quantity of sodium glyco-cholate was obtained (British Drug Houses) and tested.

[*] W. McC. Lewis, Phil. Mag. **xv.** p. 499 (1908), & xvii. p. 466 (1909).

The result is shown in fig. 6. The curve resembles that obtained for sodium oleate. The positive charge is reversed at a concentration of about 1 g./10^6 c.c. and attains a maximum negative value at about 15 or 20 g./10^6 c.c. It changes sign again (not shown on curve) at 340 g./10^6 c.c. and goes increasingly positive, the positive charge being, at a concentration of 1 g. per 100 c.c., 25 per cent. higher than that of pure water.

In view of these results, there can hardly be any doubt that the abnormal electrical effects obtained by us are

Fig. 6.
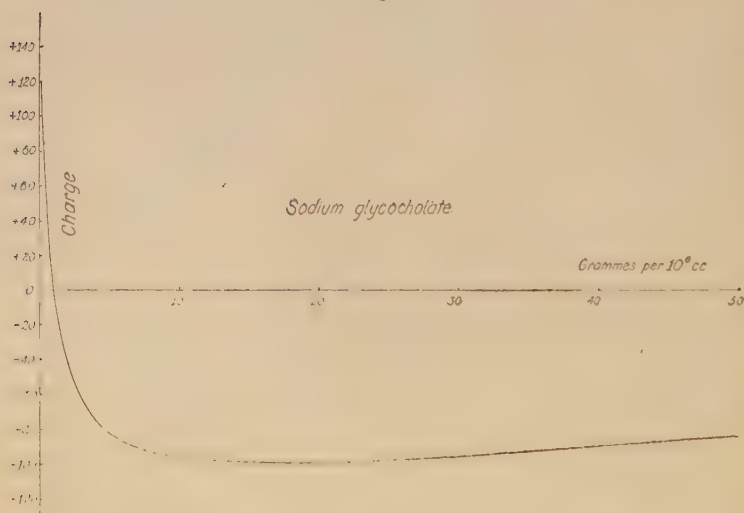
connected with the abnormal adsorptions found by Lewis. Lewis speculates as to the existence of an electrical effect of some kind in the surface layer, but rejects this explanation of the anomalous adsorption, as he considers that it should also manifest itself in the case of other electrolytes, such as the ordinary inorganic salts. The experiments just recorded show that the electrical surface conditions in solutions of these substances must be very different indeed from those prevailing in an ordinary electrolyte.

Examination of other Substances.

Other substances were examined, but the effects were not so marked as in the case of those just dealt with. The results are given briefly below.

Glycerine.—The following values were found for solutions of glycerine :—

					Charge.
Distilled water					+115
·625 g. glycerine to 100 c.c. water					+127
1·25 ,,	,,	,,	,,	....	+140
2·5 ,,	,,	,,	,,	....	+155
5·0 ,,	,,	,,	,,	....	+164
10·0 ,,	,,	,,	,,	....	+170

Starch.—A very weak solution increased the positive charge of water slightly. For concentrations higher than 1 g./litre the charge diminished.

Eosin.—The positive charge was reversed at a concentration of 8·5 g. 10^5 c.c. With increasing concentration solutions remained negative as far as tested (1 g./litre).

Fluorescene.—Positive charge was reversed between ·5 and 1 g./litre.

Picric Acid.—Positive charge was reversed at ·25 g./litre. Stronger solutions were very faintly negative.

Possible Effects of very active Substances occurring as Impurities.

The effect which such substances as sodium oleate produce when present in minute proportions shows the necessity for strict attention to the purity of all solutions. The impurity may arise in a most unexpected form and in a form not detectable by ordinary chemical methods. For example, on one occasion we found it necessary to filter a solution, and suspicion was aroused as to whether the filtering had not affected the electrical activity. We tested the filter-paper by allowing distilled water to filter through it into our spraying-vessel. We found that the filter-paper reduced the charge on distilled water to 20 per cent. of its original value. This experiment was repeated with several filter-papers, all new and of good grade. The result was the same in each case. Christiansen * gives an account of experiments with filter-paper and other materials, all tending to show the great effects that may be exercised by minute traces of active substances. We may quote another instance which is very suggestive. After tests on solutions of methyl orange, traces of this substance remained in our spraying-vessel, in spite of repeated washings with distilled water. As a result, solutions of NaCl of about 1–2 g. per litre,

* Christiansen, *Ann. der Physik*, xl. p. 107 (1913).

which normally gave positive charges when tested in the usual way, were now distinctly negative. It was not until after two days of continued washing of the vessel that the usual positive charge re-appeared. Experiments of this kind show that it is very difficult to determine what is the true effect of any substance in concentrated solution. Thus, if a substance like methylene blue were present as an impurity in sodium chloride to the extent of 1 part in 30,000, it would certainly cause a solution of 30 NaCl per litre, normally positive, to show a strong negative charge, and this negative charge would increase rapidly as the degree of pulverization increased.

Our results suggest that the negative charging in the case of inorganic salts found by most workers, and found by us in the case of NaCl at high degrees of pulverization, is due to the presence of impurities. If this view is adopted, a ready explanation is found of many features of the effect which are otherwise puzzling. Thus, while both Lenard and Rey use the splashing method, the concentration of NaCl solution at which the negative charge appears is ·1 g., litre in one case and ·5 g./litre in the other. Lenard found the maximum negative charge at 65 g./litre, Rey at 10 g./litre. We do not hold that the non-appearance of the negative charge with salt solutions in our experiments is due to the fact that our solutions are any purer than those used by other workers. But if the impurity present is of the nature of sodium oleate, the adsorption experiments of Lewis show that in a falling drop the impurity will attain to a very high degree of concentration in the surface layer, thus favouring its exerting a maximum effect when the drop splashes. The formation and disruption of surface layers in the sprayer must be a much more rapid process, and the concentration of the solute at any surface momentarily formed is very much less than in the surface of a drop which forms slowly, breaks off, and then falls some distance through air, as in the splashing experiments. On these lines we readily find an explanation of the discrepancies between the results for salt solutions obtained by the two methods. It will be re- membered also that both the splashing and the spraying methods give the same results when dealing with pure water *. In the same way the results of another experiment find explanation. A strong salt solution gives a positive charge when sprayed at our ordinary spraying pressure. If the same solution is exposed in an open vessel to a strong

* J. J. Nolan, Proc. Roy. Soc. A. vol. xc. (1914).

jet of air, it is found that the liquid begins to assume a charge as soon as the jet is strong enough to bear its surface. But the charge is negative, although the degree of breaking up of the liquid surface is very much less than that produced by the sprayer. On our view, the active impurity is very strongly concentrated in the surface layer, and is exercising its maximum negative effect.

The nature of the charge developed on strong salt solutions tends to support this view. In all our work on weak salt solutions the observations are easily repeatable to a good degree of accuracy. When the routine precautions of washing out the spraying vessel, etc., are attended to, there is never any uncertainty as to the electrical readings. The case is quite different with strong salt solutions, as has been noted earlier in this paper. The following readings, for example, were taken on different days with a solution of NaCl 30 g. litre, the spraying pressure being 40 cm.: $-76, -56, -35, +9, +7, -38, -40, -30, -25$. In all cases conditions appear to be identical. There was no known contamination, yet we have not only a fluctuation in the value of the negative charge, but a change over to positive on two occasions.

These results are best explained by assuming the existence of an impurity which varies in concentration. We have experimented with solutions of highly purified sodium chloride, but so far without obtaining any satisfactory results. Our experience with filter-paper shows that ordinary chemical standards of purity do not apply here. We are inclined to think that the salt solution itself reacts on the walls of the containing vessels, or on something attached to these walls to form the impurity. It would certainly seem as if strong salt solutions were more sensitive to contamination of the vessel, as in the case of methyl orange referred to already, than distilled water. In our view there is no decisive evidence that a pure solution of an ordinary inorganic substance ever assumes a negative charge when broken up in air.

We do not think it useful, at present, to attempt a theoretical interpretation of these effects. We have good reason for believing that electrolytes alone are active; that ordinary electrolytes act in a simple way to reduce the charging due to pure water; that certain electrolytes, in each of which one of the ions is very complex (in four cases the negative ion, in one the positive ion), produce notable effects accompanied by change of sign in dilute solutions; that these same substances are distinguished by abnormal

adsorption effects. Further experimental work is necessary before we can hope to understand the mechanism of these phenomena.

Summary.

Part I.

1. The substances ordinarily present in rain, sodium chloride excepted, will not appreciably diminish the charge produced when a rain-drop is broken in air.

2. The amount of sodium chloride present in rain in maritime districts will produce a considerable reduction.

Part II.

1. Inorganic salts in increasing concentration diminish the positive charge produced when water is broken.

2. Non-electrolytes do not affect the development of charge.

3. A group of substances shown by Lewis to give abnormal adsorption effects have a great influence on the sign and magnitude of the charge at very low concentrations.

4. It is suggested that certain results on inorganic salts obtained by other observers are due to the presence of impurities.

XXV. *An Investigation of the Angle of Contact between Paraffin Wax and Water. By* R. Ablett, *M.Sc , George Holt Physics Laboratory, University of Liverpool* *.

THE primary objects of this research were
　　(1) to devise a more accurate method of determining the contact angle ;
　　(2) to investigate the differences in the angle of contact
　　　　(*a*) when the liquid has previously been in contact with the solid,
　　　　(*b*) when there has been no previous contact.

A difference was expected between the angles in cases (2*a*) and (2*b*), and it was hoped that this would throw some light on the acknowledged difference in the lengths of the column of liquid in a capillary tube according as there is a rising or a falling meniscus. It was also hoped to throw some light on

the phenomenon of " wetting," which seems to be such an important factor in lubrication and ore concentration by the method of flotation.

The method consists essentially in immersing a cylinder, with its axis horizontal, to such a depth that the free liquid surface is plane right up to the line of contact with the curved surface of the cylinder. It is clear that in such a position the tangent plane to what would under other conditions be the curved portion of the free surface must coincide with the tangent plane to the curved surface of the cylinder at the line of contact. Then if h be the height of the free liquid surface above the lowest generator of the cylinder, and d be the diameter of the cylinder, it can easily be shown that $\cos \theta = \left(2\dfrac{h}{d} - 1 \right)$, where $h > \dfrac{d}{2}$ gives acute angles, and $h < \dfrac{d}{2}$ gives obtuse angles.

Since the distinction between a rising and a falling meniscus is primarily that of direction of relative motion of the liquid and solid. the phenomenon can be reproduced by keeping the liquid stationary and imparting motion to the solid. Accordingly an apparatus was devised for rotating the cylinder either clockwise or anti-clockwise about its horizontal axis, the former corresponding to the liquid leaving the solid, *i. e.* to a falling meniscus, and the latter to the liquid encroaching on the solid, *i. e.* to a rising meniscus. It seemed probable that the difference between the angles of contact in the two cases would depend on the relative velocity, so a reduction gear capable of variation was devised.

Apparatus.

In the final condition the apparatus is shown in fig. 1. A is a solid glass cylinder about 3 in. diam. and 3 in. long.

It is supported by the conical ends of the steel screws B, B′, which fit into small holes, about 1 mm. diam. and 1 mm. deep, at the centre of the end faces of A. The screws B, B′ fit into a solid brass support D D′, 1 in. by $\frac{1}{4}$ in., which is screwed on to the under face of the wooden top E. C is a brass wheel with a rubber tyre acting as a friction wheel on the cylinder. The axle of C passes through a brass sleeve K and the support D, and is screwed on to the pulley wheel L. The collar H and the sleeve K limit the lateral movement of C. The wooden top E fits tightly on the top of a rectangular glass tank. The whole is so arranged that the axis of A is horizontal and parallel to the long faces of the tank.

G is a glass tube connected by a flexible rubber tubing to a large aspirator bottle used as a reservoir for the water. The flow of the water is regulated by means of the tap M. The thermometer T gives the temperature of the water to $0°.1$ C. F F' is a siphon manometer of glass tube about 1 cm. diameter. The motion is supplied by means of a small electric motor, and is varied by means of a band reduction gear assisted by a variable resistance in parallel with the motor.

Fig. 1.
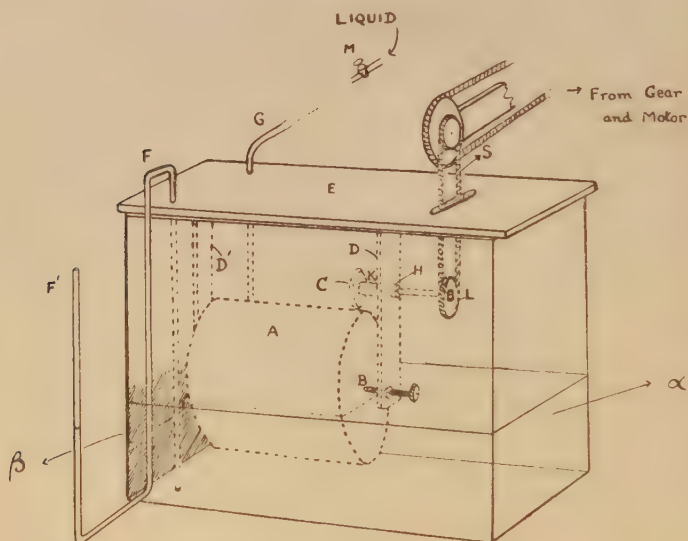
At first great difficulty was experienced in preventing the transmission of vibration through the various belts to the cylinder, and hence to the water surface. As the belt S was the only connecting link between the gear mechanism and the pulley L, rubber bands and rubber cord of various grades were tried, but without success. Finally it was found that by substituting a closely wound helical spring adjusted to a suitable tension, vibration was eliminated, and the power necessary to rotate L and the cylinder A was transmitted. The large box on which the tank stood was supported on three rubber pads to prevent the transmission of vibration from the floor.

Experimental Details.

The curvature of the water/air surface was tested by using the surface as a mirror to reflect a narrow parallel beam of

light. As in preliminary trials it was found that the angle
of contact for paraffin-wax and water was greater than 90°,
the under face of the water/air surface was used as a reflector,
thus making it possible to test the surface *right up* to the
line of contact with the cylindrical surface. (For $\theta < 90°$,
the upper face of the surface would be better.) The surface
was viewed from the right-hand side of the tank (α) in fig. 1.
The left-hand side (β) was covered with dull black paper,
with the exception of a narrow horizontal slit—1 mm. wide
approx.—about 1·5 cm. above the level of the bottom of the
cylinder. Parallel to the end (β) of the tank and distant
about 10 cm. was clamped a similar slit illuminated by a
filament lamp. Thus a shallow parallel beam of light could
be directed on the under face of the water/air surface at any
part desired, by raising or lowering the lamp and second slit.
By this means the light was made to fall on the surface at
the same vertical section of the cylinder for different levels
of water.

The level of the water was read by means of a microscope
focussed on the meniscus in the manometer tube F, which
was backed by a mm. scale. The microscope eyepiece was
graduated to 0·1 mm.

The glass tank, tubing, and reservoir were cleaned by
alternately scrubbing half-a-dozen times with concentrated
nitric acid and warm potassium bichromate solution, and
then washing vigorously in tap water. The rubber tubing
had steam passed through it for three hours, and was then
left soaking in tap water.

To coat the cylinder with wax, the pulleys L and C, with
their axle, were removed from the support D D′. The
cylinder was then slightly immersed in a dish of molten
wax and slowly spun until a coating about 3 or 4 mm. thick
was deposited. It was then placed in a closed fume-chamber
to cool. It was afterwards centred accurately in a lathe and
turned smooth. Its diameter was measured by vernier
callipers, three readings being taken at intervals of approxi-
mately 60°. The mean value was taken as d.

Method of Procedure.

CASE I.—*Cylinder stationary.* Giving θ.

The cylinder A and pulleys C and L with axle were now
replaced in the apparatus, and the tap M opened. Water
from the tank was sucked into the siphon F F′. An electric
lamp was placed behind the tank (fig. 1) at about the level

of the bottom of the cylinder, and the tank viewed from in front. The lowest generator of the cylinder and its image in the upper surface of the water were observed gradually approaching as the water-level rose. When they had approached to within about 2 mm., the rate of inflow of the water was cut down by the tap M. When the generator and its image just touched, the tap was closed. It was observed that immediately this happened, the water jumped up the wax surface to a height of 1–1·5 mm., owing to the fact that here the angle between the tangent plane to the cylinder and the general surface of the water was greater than the angle of contact. The reading on the manometer was taken. It appears as A in the tables of results.

The lamp was replaced behind the slits and the tap opened. The image of the slit on face β) in the lower face of the air/water and water wax surfaces was then carefully observed through the end (α) of the tank.

At first, when the air/water surface was convex downwards, as in fig. 2 (*a*), the meniscus portion behaved as a convex mirror to the incident light, and the line of contact of air/water/wax appeared as in fig. 2 (*b*). On

Fig. 2.

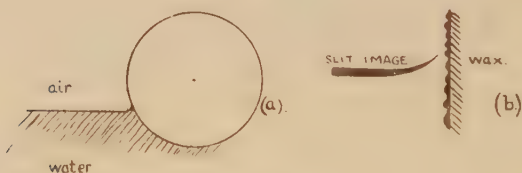Fig. 3.

still raising the water-level slowly, the image gradually straightened out and extended right up to the line of contact, and the blurs with their light contours due to slight irregularities in the wax reduced to a minimum. The air/water surface was then regarded as a horizontal plane. The second slit and the lamp had been lowered so that the light was still incident on the same vertical

section of the cylinder as before. The height of the water in the manometer was read, giving readings B. The difference (B—A) gave the value h.

From this the value of $\theta = \cos^{-1}\left(2\dfrac{h}{d}-1\right)$ was calculated.

This value, θ, is the angle of contact as generally accepted.

CASE II.—*Cylinder rotated anti-clockwise.* Giving θ_1.

With the water-level corresponding to the value θ (Case I.), if the cylinder were rotated anti-clockwise the meniscus on the left of the cylinder became convex upwards, corresponding to an increase in the value of the contact angle; whilst that on the right became concave upwards, corresponding to a decrease in the angle.

The former case is analogous to a rising meniscus and the latter to a falling meniscus.

The left-hand side was always observed.

The water-level was lowered by placing the reservoir lower than the tank and opening the tap M. At first the appearance of the image of the slit and line of contact of air/water wax was as in fig. 3 (*b*), the water/air surface near the wax acting as a concave mirror. As the water-level was lowered, the widening-out of the image diminished, and the light along the contour decreased to a minimum. At a critical level a perfect image was seen right up to the line of contact. The tap M was closed and the motion stopped. The level B was read on the manometer. (B—A), as before, gave AB = h, and the value of $\cos^{-1}\left(2\dfrac{h}{d}-1\right) = \theta_1$ was calculated.

This gave θ_1, the maximum value of the contact angle for the corresponding speed of rotation.

By stopping the motor immediately a value of B was obtained, it was possible to obtain several readings with the portion of the surface which had not been wetted.

CASE III.—*Cylinder rotated clockwise.* Giving θ_2.

The motion was reversed by replacing the belt from pulleys to Z by a crossed belt. The same procedure as in Case II. was adopted, except that, as the meniscus was at first concave upwards, the reservoir had to be placed higher than the tank so that the water-level could be raised. The same number of readings was taken as in Case II.; but in order that they might be taken in pairs

according to the portion of the wax surface at the line of contact, the readings were set down in the table in the reverse order: the first reading here corresponds to the last reading in Case II., and so on.

In this case, $\cos^{-1}\left(2\dfrac{h}{d}-1\right) = \theta_2 =$ minimum value of contact angle for this speed.

Values of θ were determined before and after each complete set of θ_1 and θ_2. The temperature of the water was also taken before and after the experiments, and the mean value taken.

TABLE I.

$d = \left\{\begin{array}{l} 7\cdot75 \\ 7\cdot75 = 7\cdot75 \text{ cm.} \\ 7\cdot75 \end{array}\right.$ Initial Temp. $= 10°\cdot3$ C. $\left.\begin{array}{l} \\ = 10°\cdot5 \text{ C.} \end{array}\right\}$ Mean Temp. $= 10°\cdot4$ C.

1 revolution of Cylinder in 303 secs.

$\therefore \quad v = 0\cdot8036$ mm./sec.

A.	B.	$AB = h$.	$\left(2\dfrac{h}{d}-1\right)$.	$\cos^{-1}\left(2\dfrac{h}{d}-1\right)$.	$\left(\dfrac{\theta_1+\theta_2}{2}\right)$.	$(\theta_1+\theta_2)$.
3·935	6·310	2·375	−·3871	112° 47′		
,,	7·380	3·445	−·1110	96° 22′	104° 35′	16° 25
,,	6·285	2·350	−·3935	113° 10′		
,,	7·390	3·455	−·1084	96° 13′	104° 42′	16° 57′
,,	6·30	2·365	−·3897	112° 56′		
,,	7·395	3·460	−·1071	96° 9′	104° 33′	16° 47′
,,	6·310	2·375	−·3871	112° 47′		
,,	7·390	3·455	−·1084	96° 13′	104° 30′	16° 34′
,,	7·305	2·370	−·3884	112° 51′		
,,	7·385	3·450	−·1097	96° 18′	104° 35′	16° 33′
,,	6·290	2·355	−·3923	113° 6′		
,,	7·38	3·445	−·1110	96° 22′	104° 44′	16° 44′
3·935	6·84	2·905	−·2503	104° 30′		
3·935	6·835	2·90	−·2516	104° 34′		

Mean .... $\theta = 104°$ 32′

,, ... $\theta_1 = 112°$ 56′ $\therefore \quad \frac{1}{2}(\theta_1+\theta_2) = 104°$ 36′

,, ... $\theta_2 = 96°$ 16′ $\therefore \quad (\theta_1-\theta_2) = 16°$ 40′

The speeds of rotation were determined by timing one complete revolution of the cylinder by means of a stop-watch.

After a complete set of readings of θ, θ_1, and θ_2 at a given speed, the cylinder was scraped and then recoated and turned, and the tank and tubing washed with tap water. When not in use, the tank and tubing were left in running water.

Table II.

Summary of Mean Values.

The figures in line I. are the mean values from Table I., and so on.

	v. mm./sec.	$-\cos\theta_1$.	$-\cos\theta_2$.	$-\cos\theta$.	θ_1. ° ′	θ_2. ° ′	θ. ° ′	$\frac{1}{2}(\theta_1+\theta_2)$. ° ′	$(\theta_1-\theta_2$ ° ′
I.	0·1273	·3321	·1663	·2513	109 24	99 34	104 33	104 29	9 50
II.	0·1943	·3506	·1522	·2517	110 31	98 45	104 34½	104 38	11 46
III	0·3113	·3769	·1234	·2497	112 8½	97 5	104 28	104 37	15 3
IV.	0·441	·3933	·1114	·2494	113 10	96 22	104 25	104 46	16 48
V.	0·641	·3904	·1097	·2516	112 59	96 18	104 34	104 38½	16 41
VI.	0·8036	·3897	·1093	·2510	112 56	96 16	104 32	104 36	16 40
VII.	1·06	·3935	·1087	·2513	113 10	96 15	104 34	104 42⅔	16 55
VIII.	1·472	·3920	·1110	·2523	113 5	96 23	104 37	104 44	16 42
IX.	1·969	·3940	·1104	·2516	113 13	96 20	104 34	104 46	16 53
X.	2·378	·3977	·1090	·2516	113 26	96 16	104 34½	104 51	17 10
XI.	2·43	·3936	·1148	·2501	113 11	96 36	104 29	104 53	16 35
XII.	3·586	·3918	·1127	·2532	113 4	96 29	104 49	144 46	16 35
XIII.	3·926	·3948	·1063	·2523	113 15	96 6	104 36½	104 40	17 9

In lines IV. to XIII. it is obvious that θ_1, θ_2, $\frac{1}{2}(\theta_1+\theta_2)$, and $(\theta_1-\theta_2)$ are constant.

Thus for speeds $> \cdot44$ mm./sec. (taking the average values):

$$\theta_1 = 113° 9',$$
$$\theta_2 = 96° 20',$$
$$(\theta_1-\theta_2) = 16° 49'.$$

The wax used was a specimen of Kohlbaum's Purified Paraffin-Wax of melting-point 56°·7 C., being the mean of six determinations lying between 56°·6 C. and 56°·85 C. The author is indebted to Professor I. M. Heilbron for the specimen.

Discussion of the Results.

The following are the results obtained for water at 10° C. :—

Angle of contact θ when the cylinder
    is stationary . . . . $= 104^\circ\ 34'$,
    being the mean of thirty observations lying between
    $104^\circ\ 21'$ and $104^\circ\ 52'$, twenty of the readings lying
    between $104^\circ\ 30'$ and $104^\circ\ 40'$.

A specimen set of observations taken whilst the cylinder was in motion is given in Table I.

In all, observations were made at thirteen different speeds, the results being summarized in Table II. and Graph I. The values of θ_1, θ_2, $\frac{1}{2}(\theta_1 + \theta_2)$, $(\theta_1 - \theta_2)$ there given are the mean values at the stated speed, whilst θ is the mean of readings taken before and after the experiment.
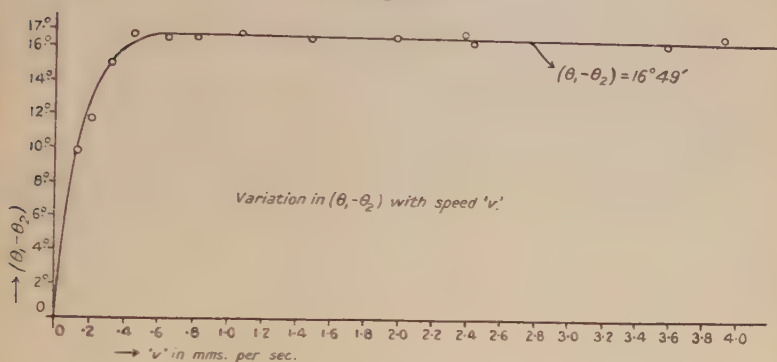
Graph I.

Angle of Contact for Water and Paraffin Wax — Variation with Relative Motion
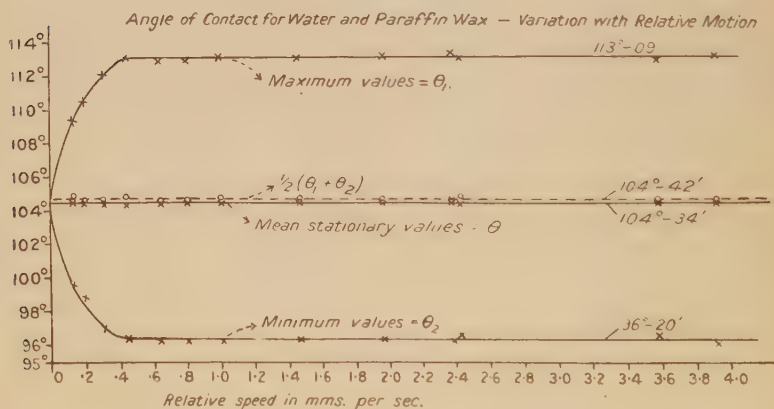
Graph I. shows very clearly that at all speeds the maximum value of the contact angle θ_1 and the minimum value θ_2 are equidistant from the stationary value θ; and that $\frac{1}{2}(\theta_1 + \theta_2)$ agrees, within the range of experimental error, with the value θ. It is also clear that for speeds > 0.44 mm./sec., both θ_1 and θ_2 are constant, being equal to $113^\circ\ 9'$ and $96^\circ\ 20'$ respectively. It is therefore concluded that there exists both a maximum and a minimum angle of contact, in addition to the angle of contact θ usually found, their values in the case of paraffin-wax and water being as stated above.

Graph II. shows the change in $(\theta_1 - \theta_2)$ with v, again pointing to the same conclusion.

Graph II.

$(\theta_1 - \theta_2) = 16° 49'$

Variation in $(\theta_1 - \theta_2)$ with speed 'v.'

$\rightarrow v$ in mms. per sec.

Possible Error.

The possible error amounted to a difference of ·005 cm. in the value of $h = AB$, which leads to a possible error of ± 5 minutes in the angles.

Thus it may be taken that

$$\theta = 104° \; 34' \pm 5',$$
$$\theta_1 = 113° \quad 9' \pm 5',$$
$$\theta_2 = 96° \; 20' \pm 5'.$$

The average deviations from the mean values are: for $\theta = 3'$, $\theta_1 = 6'$, and $\theta_2 = 6'$.

The only other results for paraffin-wax and water within the knowledge of the writer are: $\theta = 105°$ (Coghill and Anderson, "Molecular Physics of Ore Flotation," J. Phys. Chem. xxii. p. 249, April 1918), and $\theta = 106° \; 57'$ as the means of four values ranging from 106° 8' to 107° 41' by the depression of water in a waxed tube and $\theta = 106° \; 28'$ by the tilting-plate method (Hartley and Bosanquet, Phil. Mag. No. 249, Sept. 1921, p. 458).

Conclusion.

Various writers have noted a difference between the heights of the liquid in a capillary tube according as there is a rising or a falling meniscus; others, a difference between the thicknesses of drops of the same size according as the drops are expanding or contracting. The results here given provide an explanation of these differences.

Harkins and Brown, in "The Determination of the Surface Tensions of Water and Benzene by Capillary Height Methods" (Journ. Amer. Chem. Soc. xii. p. 499), state : " The rise for a falling meniscus was always greater than for a rising meniscus in the same sample of water, so *only the former was used*."

In the case of these liquids, $\theta_2 = 0$ but θ_1 does not, as there will be a finite maximum angle, though it may be small. In the falling meniscus, where the walls have been in previous contact with the liquid, $\theta_2 = 0$; but in the rising meniscus the contact angle is not θ_2, but θ_1 and finite.

Thus $\cos \theta_1$ is $< \cos \theta_2$, and therefore $T \cos \theta_1 < T \cos \theta_2$; and therefore the height in the falling meniscus case will be greater than for the rising meniscus in the ratio $\cos \theta_2 : \cos \theta_1$.

Allan Ferguson, in "Studies in Capillarity—II." (Faraday Soc. Trans. Feb. 1921), dealing with a method of adjusting the air-pressure to force the meniscus down to the level of the free liquid surface, says :—" The presence or absence of a constant error was tested by taking the mean of the readings, (1) when the meniscus just disappeared within the tube, (2) when it just protruded from the tube. The mean of these pressures agreed satisfactorily with the ' crucial ' pressure."

The results given in the present paper explain this. Taking for granted that $\theta_2 = 0$ for water, θ_1 finite but small, then, as before, $T \cos \theta$ should agree with $\left(\dfrac{T \cos \theta_1 + T \cos \theta_2}{2} \right)$.

Many writers insist on the necessity for tapping the capillary, or the plate on which a drop rests, before taking readings, but give no reason beyond that it pays to do so— *e. g.*, Hartley and Bosanquet, in the paper already cited, when determining θ for water and azobenzene by the measurement of a drop, state : " The necessity for tapping the plate is shown by the following two readings taken without tapping :—

Expanding drop . . 0·396 cm., ⎫ (Thickness of
Contracting drop . . 0·270 cm." ⎭   the drop.)

Here again, in the expanding drop, the water is creeping over fresh solid surface, and the angle of contact is the maximum θ_1, whilst in the contracting drop the angle to be taken is the minimum θ_2. The result obtained by tapping would correspond to θ and would be the same as the

mean of the results θ_1 and θ_2, since it has been shown that $\theta = \frac{1}{2}(\theta_1 + \theta_2)$. In fact, the mean of the two readings given—0·333 cm.—agrees with the mean value obtained by tapping as used by the writers named, viz. 0·335 cm.

Note on Wetting.

Notwithstanding that "wetting" has become such an important factor in connexion with the Flotation of Minerals and also in lubrication, the term is often used in a very loose manner. The writer has not been able to obtain a definite statement as to the meaning of "wetting." Many writers tacitly assume that a liquid that "wets" a solid makes with it a zero contact angle. *Cp.* Edser, 'General Physics,' p. 312, and Richards & Carver (Journ. Amer. Chem. Soc. xliii. 1921, p. 827 *et seq.*). Others assume that a liquid "wets" a solid when $\theta < 90°$, and does not "wet" it when $\theta > 90°$.

Clerk Maxwell, in the article on Capillarity in the Encycl. Brittanica, states the question thus :—"If a small quantity of a fluid stand in a drop on the surface of a solid without wetting it, the angle of contact is 180°; if it spreads over the surface and wet the solid, the angle of contact is zero."

With regard to this statement, there is no known combination of liquid and solid where $\theta = 180°$ (unless the solid surface be dusty); thus, in Maxwell's sense, there is no case where the fluid rests on the solid without wetting it. On the other hand, most combinations of liquid and solid give a value of θ intermediate between $0°$ and $180°$. The cases might therefore be distinguished as "non-wetting" ($\theta = 180°$), "partial wetting" (θ finite), and "complete wetting" ($\theta = 0$). Still this does not give any real physical significance to the term "wetting."

From the fact that θ_1 is $> \theta_2$, it follows that the surface energy of the air/solid interface has been increased by having been in contact with the liquid. From this it is concluded that the solid has absorbed or imbibed some of the liquid. It then follows that if the solid be moved relative to the liquid in a direction tangential to the interface, for example by a clockwise rotation of the waxed cylinder in the experiments previously described, that portion leaving the liquid will tend to drag the liquid with it up to the limit of the force of cohesion of the liquid or of the adhesion between liquid and solid, whichever is the greater. Thus the contact angle on the leaving

side will be decreased towards θ_2 and that on the entering side increased towards θ_1. When separation does take place, the contact angle in the former case will be the minimum value θ_2, and in the latter case the maximum value θ_1, for that particular speed.

Thus the results obtained strongly support the view that this variation in the contact angle is due to absorption or imbibition of the liquid by the solid. Such a phenomenon is true "wetting," and, as is evident from these experiments, is possible for obtuse as well as acute angles of contact—degree of wetting depending on the range $(\theta_2 - \theta_1)$, that is to say on the degree to which the surface energy of the solid is affected on coming into contact with the liquid.

These experiments are to be repeated with other combinations of solids and liquids.

XXVI. *The Second Virial Coefficient of Gases. By* Angus F. Core, *Chemical Department, The University, Manchester* [*].

Chemical Department, The University, Manchester [*].

THE equation of state of a perfect gas is $pv = RT$, where p is the pressure, v the volume occupied by the unit of quantity, T the absolute temperature, and R the gas constant for the unit of quantity. This is a limiting relation which we may suppose that the behaviour of all real non-dissociating gases approaches as the volume becomes very great.

The equation of state of any gas may be written in the form

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \ldots,$$

where A, B, C, etc. are called the first, second, third, etc. virial coefficients. These coefficients are functions of T but not of v. The value of A for a non-dissociating gas, with which only are we concerned, is necessarily RT; the same for the gram molecule of all gases.

It is the object of the present discussion to deduce the value of the second virial coefficient, in the first place of a gas with molecules of a spherically symmetrical type, and then of a gas with molecules of a general type. In the very special case of a gas consisting of hard spherical molecules exerting no attraction on each other, the third coefficient, C, is readily found. The results agree with those obtained by Keesom [*] and others, but the method is comparatively simple.

The kinetic significance of what is known in thermo-dynamics as "activity" is shown in the paper.

In the last section an expression has been obtained for the second virial coefficient of a binary mixture of gases.

Preliminary.

Suppose that in a vessel of unit volume, kept at a uniform temperature T, there are ν molecules of a gas. Then if the molecules are non-attracting mass points, and if no external forces act on them, except those exerted by the walls of the containing vessel, the molecular concentration is every-where ν. By this statement it is not meant that in any volume element, dr, there are $\nu\,dr$ molecules, since, evidently, the chances are against there being any of the molecules in the particular element at a given instant. What is meant is that the probability of there being one molecule in the element dr at any instant is $\nu\,dr$. That is to say, if we could take a very large number, A, of instantaneous views of the element dr we should observe a point molecule in it $A\nu\,dr$ times : or if there were A exactly similar unit vessels each containing ν molecules, then at any instant there would be $A\nu\,dr$ of them with a molecule in a particular element dv.

Suppose, now, that external forces act on the molecules, of a kind that can be derived from a permanent field of potential. Then the molecules will no longer be distributed uniformly over the unit volume. If the work required to bring a single molecule from a region taken to be of zero potential to a given point is χ, then χ is the potential at that point, and according to the classical theory of statistical mechanics the molecular concentration there is equal to

$$\nu_0 e^{-\chi/kT},$$

where T is the temperature and k the gas constant per molecule. Putting $\chi=0$ it will be seen that ν_0 is the molecular

* W. H. Keesom, Proc. Sect. of Sciences, Amsterdam, vol. xv. (1) pp. 240, 256.

concentration in regions of zero potential. In this expression χ is the potential due to an external field which does not vary with the time. This result can be extended in the following way.

Let the molecules be such that they exert forces on each other depending only on the distances separating their centres. Then round each centre there is a field of potential with respect to another molecule. The instantaneous potential, χ, at any point, due to another molecule or other molecules, is defined to be the work required to bring the centre of a single molecule from a region of zero potential up to that point while the other molecule or molecules are kept fixed in position. Consider, then, the ν molecules at any instant. They are in definite positions and consequently there is a definite instantaneous potential with respect to another single molecule. Let another molecule be added to the vessel, so that there are now $\nu + 1$ molecules. Then if we regard only those moments in the history of the first ν molecules in which they have these same positions, it is shown by statistical mechanics that the probability that the centre of the single molecule is in an element of volume dv, where the instantaneous potential is χ, is proportional to

$$e^{-\chi/kT}\, dv,$$

just as when the field is a permanent external one.

The theorem may be further extended so as to include molecules which exert forces on each other depending not only on the distance separating them but also on their orientations in any way. Just as before, we choose instants when the ν molecules are always in the same positions, not now as regards only the points taken as their centres, but also as regards their exact orientations. We cannot now speak of the potential of the remaining molecule at any point, for this does not depend only on the position of the molecule's centre, but also on its orientation. Nevertheless, it is shown that if we further restrict the instants of viewing the system to instants when the single molecule is orientated in a particular way, then the probability of its centre being in the element of volume dv is proportional to

$$e^{-\chi/kT}\, dv,$$

χ being the now perfectly definite quantity of work required to bring the centre of the single molecule orientated in this definite way into the element of volume dv.

Spherically Symmetrical Molecules.

Imagine a single molecule in a vessel of unit volume, this volume being very large compared with the molecular field. Then if the potential throughout the vessel is uniform, the probability that at any instant the centre of the molecule lies in an element of volume dv is equal to dv. The molecular concentration is everywhere equal to 1.

Now suppose that there are ν other identical molecules in the vessel. Then if we regard the first molecule only at those instants when the other ν molecules are always in the same positions, its concentration is no longer uniform but is equal to

$$P_0 e^{-\chi/kT},$$

where χ is the instantaneous potential due to the other molecules, and P_0 is the concentration in regions of zero potential, which will be taken to be those regions outside the field of any molecule. It is evident that, since this concentration refers to one molecule in a vessel of unit volume, if it be integrated with respect to the volume over the whole unit volume the result must be 1. Therefore for finding P_0 we have the equation

$$P_0 \int e^{-\chi/kT}\, dv = 1,$$

the integration being taken over the whole interior of the vessel. Now, outside the field of a molecule the potential χ is zero, and therefore

$$(1 - e^{-\chi/kT}) = 0.$$

Therefore the above equation is conveniently put into the form

$$P_0 \int \left\{ 1 - (1 - e^{-\chi/kT}) \right\} dv = 1.$$

This is equivalent to

$$P_0 \left\{ 1 - \int (1 - e^{-\chi/kT})\, dv \right\} = 1,$$

since the integration is through a unit of volume. Thus

$$P_0 = \frac{1}{1 - \int (1 - e^{-\chi/kT})\, dv}.$$

This, therefore, gives the concentration of the single molecule at all points outside the influence of any other molecule for a particular arrangement of these other molecules. Now in any real case ν is very large and the statistical arrangement of the molecules practically never varies appreciably from

a certain most probable arrangement. Consequently we may assume that

$$\int (1 - e^{-\chi/kT}) dv$$

does not vary with the time. Therefore we may write

$$\int (1 - e^{-\chi/kT}) dv = f(\nu,\ T),$$

$f(\nu,\ T)$ being a function of ν and T only, for a given kind of molecule. Thus the presence of the other ν molecules raises the concentration of the first molecule in regions of zero potential from 1 to

$$\frac{1}{1 - f(\nu,\ T)}.$$

Now, since all the molecules are exactly alike, it is evident that this applies to each one of them. Therefore the total concentration of the molecules in regions of zero potential must be given by

$$\nu_0 = \frac{\nu + 1}{1 - f(\nu,\ T)} \quad \text{or} \quad \frac{\nu}{1 - f(\nu,\ T)},$$

since $\nu + 1$ is indistinguishable from ν.

The evaluation of $f(\nu,\ T)$ in any particular case is the chief difficulty of the problem. ν_0 and ν are converted into the corresponding gram molecular quantities, A and C, by the substitutions $A = \nu_0/N$, $C = \nu/N$, in which N is the number of molecules in the gram molecule. Thus

$$A = \frac{C}{1 - f(\nu,\ T)}.$$

Before considering the value of $f(\nu,\ T)$ we shall obtain a relation by means of which the pressure may be calculated when the concentration, C, and A are known.

The required relation is obtained directly as follows :—Imagine a column of the gas standing in the gravitational field of the Earth. Let " z " be the height measured above any given level. Then if " m " is the mass of a single molecule, we have the hydrodynamical relation

$$dp = CNmg\,dz. \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Now in general there are two sorts of field acting simultaneously on the molecules: the gravitational field and the inter-molecular fields. A is the concentration outside the inter-molecular fields and therefore in regions where the potential is that due to the gravitational field alone. This

potential is equal to mgz. Therefore the value of A at any height z is given by

$$A = A_0 e^{-mgz/kT}.$$

Therefore

$$kT\, d \log A = mg\, dz, \quad \text{or} \quad RT\, d \log A = Nmg\, dz, \quad (b)$$

where R is the gas constant per gram molecule. Combining (a) and (b) we obtain the required relation

$$\frac{dp}{C} = RT\, d \log A.$$

It may be noticed that this result enables us to identify A with the quantity known in thermodynamics as the "activity" of the gas.

Since

$$A = \frac{C}{1 - f(\nu, T)}.$$

Therefore

$$\frac{dp}{C} = RT\, d \log \frac{C}{1 - f(\nu, T)}.$$

If then we can find the value of $f(\nu, T)$ the integration of this equation will yield the value of the pressure.

Now

$$f(\nu, T) = \int (1 - e^{-\chi/kT})\, dv,$$

the integration being taken over the whole interior of a vessel of unit volume containing ν molecules, and χ being the instantaneous potential due to these molecules. $f(\nu, T)$ is a very difficult quantity to calculate for the following reason. Although $(1 - e^{-\chi/kT})$ is very small except quite close to a molecule, nevertheless at any instant some molecules will be close enough to one or more other molecules to cause parts of their fields where the potentials are not small to overlap. This makes the evaluation of the integral in the above equation exceedingly difficult.

But when the gas is not too concentrated it is allowable to neglect the overlapping of molecular fields in this estimation; or at any rate of the overlapping of those parts where the potentials are not small. The error so introduced will not affect the second virial coefficient, being of the same order of magnitude as the third coefficient. To this degree of approximation, therefore, we may write

$$f(\nu, T) = \nu \int (1 - e^{-\chi/kT})\, dv = \nu \phi(T),$$

the integration being taken not over the whole interior

of the vessel but over the field of a single molecule.
$\phi(T)$ is, for a particular kind of molecule, a function of
the temperature only.

Write $\Phi(T) = N\phi(T)$. Then

$$A = \frac{C}{1 - C\Phi(T)}.$$

Therefore, for finding the pressure, we have the relation

$$\frac{dp}{C} = RT \, d\log \frac{C}{1 - C\Phi(T)}.$$

The solution of this gives

$$p = -\frac{RT}{\Phi(T)} \log\left(1 - C\Phi(T)\right). \quad . \quad . \quad . \quad (c)$$

If the interference of molecular fields had not been neglected,
instead of $\Phi(T)$ we should have obtained a series of ascending
powers of C :

$$\Phi_1(T) + \Phi_2(T)C + \Phi_3(T)C^2 + \ldots .$$

Therefore to the required degree of accuracy the relation (c)
is equivalent to

$$p = RTC + \tfrac{1}{2}RTC^2\Phi(T). \quad . \quad . \quad . \quad (d)$$

The expression for the pressure given in (c) is interesting
inasmuch as in obtaining it the only error made has been the
neglect of the simultaneous approach of three or more mole-
cules. The error of assuming uniform concentration up to
the wall of the containing vessel has not been made. The
two errors are, however, of the same order of magnitude.

If we compare (d) written in the form

$$pv = RT + \frac{RT\Phi(T)}{2v} \quad \text{with} \quad pv = RT + B/v,$$

it will be seen that the second virial coefficient is given by

$$B = \tfrac{1}{2}RT\Phi(T).$$

The function $\Phi(T)$, that is

$$N \int \left(1 - e^{-\chi/kT}\right) dv,$$

must be evaluated for any particular type of molecule by
writing for χ the corresponding function of the distance "r"
separating the centres of two molecules. In place of the
differential dv we substitute $4\pi r^2 dr$, and integrate from $r = 0$

to $r = \infty$; that is, to a value of r sufficiently great to make $(1 - e^{-\chi/kT})$ negligible.

We shall first consider a type of molecule that will give an equation of state, so far as the second virial coefficient, of the same form as the equations of van der Waals and Dieterici. Both these equations as far as the second order terms may be written

$$pv = RT + \frac{RT}{v} - \frac{a}{v}.$$

It will be seen on comparing this with the general expression that the term B/r in the latter is represented in this equation by two terms : one proportional to T, the other independent of T. In general this will not be the case. But suppose that from $r = 0$ to $r = \sigma$, χ/kT is very great, and that for $r > \sigma$, χ/kT is everywhere small. The integral

$$N \int (1 - e^{-\chi/kT}) dv = 4\pi N \int_0^x (1 - e^{-\chi/kT}) r^2 \, dr$$

then divides into two parts :—

$$4\pi N \int_0^\sigma (1 - e^{-\chi/kT}) r^2 \, dr, \quad \text{where } \chi/kT \text{ is very great,}$$

and

$$4\pi N \int_\sigma^x (1 - e^{-\chi/kT}) r^2 \, dr, \quad \text{where } \chi/kT \text{ is small.}$$

Therefore approximately

$$\Phi(T) = \tfrac{4}{3}\pi N \sigma^3 + \frac{4\pi N}{kT} \int_\sigma^\infty \chi r^2 dr$$

and

$$pv = RT + \frac{2RT\pi N \sigma^3}{3v} + \frac{2\pi N^2 \int_\sigma^\infty \chi r^2 dr}{v}.$$

Under these circumstances, then, B separates into two parts, one of which is nearly proportional to T and the other nearly independent of T, just as in the equation of van der Waals. This is because part of the field consists of a region of very high potential and the rest is a region of small potential. It is evident that the higher the temperature the more completely does the second part become independent of T and also that the first part becomes less closely proportional to T. Comparing the two equations it will be seen that the "b" of van der Waals equals $\tfrac{2}{3}\pi N \sigma^3$, that is 4 times the

actual " volume" of the molecules in the gram molecule ; and that the " a " of van der Waals equals

$$-2\pi N^2 \int_\sigma^\infty \chi r^2 dr.$$

In general B does not divide in this way. Thus consider the case of a gas which consists of molecules which attract or repel each other according to an inverse power of the distance separating their centres. Suppose that the molecules are perfectly hard and of diameter σ, and that for values of r greater than σ two molecules attract each other with a force proportional to $1/r^{q+1}$. Let χ_σ be the work required to separate two molecules in contact to an infinite distance apart. Then

$$\chi = \infty \qquad \text{for} \quad r < \sigma,$$

$$\chi = -\chi_\sigma \left(\frac{\sigma}{r}\right)^q \quad \text{for} \quad r \gtreqqless \sigma.$$

In this case therefore

$$\Phi(T) = 4\pi N \int_0^\sigma (1 - e^{-\chi/kT}) r^2 dr + 4\pi N \int_\sigma^\infty (1 - e^{-\chi/kT}) r^2 dr,$$

in which χ stands for $-\chi_\sigma \left(\frac{\sigma}{r}\right)^q$.

This may be integrated by expanding $e^{-\chi/kT}$ into a series of powers of χ/kT and integrating term by term. Thus

$$\Phi(T) = \tfrac{4}{3} N\pi\sigma^3 \left\{ 1 - \frac{3}{(q-3)} \frac{\chi_\sigma}{kT} - \frac{1}{2!} \frac{3}{(2q-3)} \left(\frac{\chi_\sigma}{kT}\right)^2 \right.$$
$$\left. - \frac{1}{3!} \frac{3}{(3q-3)} \left(\frac{\chi_\sigma}{kT}\right)^3 - \cdots \right\},$$

and therefore

$$pv = RT + \frac{RTb}{v} - \frac{3RTb}{v} \left\{ \frac{1}{(q-3)} \frac{\chi_\sigma}{kT} + \frac{1}{2!} \frac{1}{(2q-3)} \left(\frac{\chi_\sigma}{kT}\right)^2 \right.$$
$$\left. + \frac{1}{3!} \frac{1}{(3q-3)} \left(\frac{\chi_\sigma}{kT}\right)^3 + \cdots \right\}.$$

The solution fails when $q < 3$.

It will be observed that at temperatures sufficiently great to make χ_σ/kT moderately small the relation approximates to

$$pv = RT + \frac{RTb}{v} - \frac{3Nb\chi_\sigma}{(q-3)v}.$$

The Third Virial Coefficient for Spherically Symmetrical Molecules.

In order to calculate the third term on the right-hand side of the equation

$$pv = RT + \frac{B}{v} + \frac{C}{v^2} + \dots$$

it is necessary to integrate

$$(1 - e^{-\chi/kT}) dv$$

over all the molecular fields, taking into account the propinquity of two molecules. If this were done we should obtain for $f(v, T)$ an expression of the form $\nu\phi_1(T) + \nu^2\phi_2(T)$, and therefore instead of $\Phi(T)$ the expression

$$\Phi_1(T) + C\Phi_2(T) \quad \text{or} \quad \Phi_1(T) + \frac{1}{v}\Phi_2(T),$$

if $1/v$ be substituted for C. The activity A is therefore given by

$$A = \frac{1}{\left(v - \Phi_1(T) - \frac{1}{v}\Phi_2(T)\right)},$$

and the corresponding differential relation between the pressure and volume is

$$v\,dp = RT\,d \log \frac{1}{\left(v - \Phi_1(T) - \frac{1}{v}\Phi_2(T)\right)}.$$

The solution of this to the required approximation is

$$pv = RT + \frac{RT\Phi_1(T)}{2v} + \frac{RT}{3}\left(\frac{\Phi_1^2(T) + 2\Phi_2(T)}{v^2}\right). \quad . \quad (e)$$

To evaluate the coefficient $\Phi_2(T)$ we may proceed in the following way. Fix the attention on one particular molecule of the $\nu + 1$ molecules contained in the vessel of unit volume. The probability that a second particular molecule at any instant has its centre within a distance between r and $r + dr$ of the centre of the first molecule is with sufficient accuracy $4\pi r^2 e^{-\chi/kT} dr$. Therefore the probability that any one of the ν molecules is so situated with respect to the first is $4\pi\nu r^2 e^{-\chi/kT} dr$. Therefore the number of molecules out of the whole number in unit volume which have such a neighbour is $4\pi\nu^2 r^2 e^{-\chi/kT} dr$. Therefore the number of pairs of

molecules whose centres are separated by a distance between r and $r + dr$ is $2\pi\nu^2 r^2 e^{-\chi/kT}\,dr$.

When we integrate over the field of two molecules which are far apart, then

$$\int (1 - e^{-\chi/kT})dv = 2\phi(\mathrm{T}).$$

When r is not great this will no longer be the case, and the value of the integral taken over the combined field may conveniently be written $2\phi(\mathrm{T}) + g(r, \mathrm{T})$, in which $g(r, \mathrm{T})$ is a function of r and T depending on the molecular field. Thus every pair of molecules for which r is between r and $r + dr$ contributes to the total integral $f(\nu, \mathrm{T})$ the quantity $g(r, \mathrm{T})$ in excess of their contribution when the component molecules are far apart.

Therefore, since the number of such pairs is $2\pi\nu^2 r^2 e^{-\chi/kT}dr$, the value of $f(\nu, \mathrm{T})$ is given by

$$f(\nu, \mathrm{T}) = \nu\phi(\mathrm{T}) + 2\pi\nu^2\int_0^\infty r^2 g(r, \mathrm{T})e^{-\chi/kT}dr.$$

Therefore

$$\Phi_1(\mathrm{T}) = \mathrm{N}\int (1 - e^{-\chi/kT})dv,$$

the integration being taken over the whole field of a single molecule ; and

$$\Phi_2(\mathrm{T}) = 2\pi\mathrm{N}^2\int_0^\infty r^2 g(r, \mathrm{T})e^{-\chi/kT}dr.$$

When these two quantities have been evaluated they must be substituted in the equation (e).

If the molecules are simply hard elastic spheres of diameter σ, with no external field, $\Phi_2(\mathrm{T})$ is readily found. In this case

$$\chi = \infty \quad \text{for} \quad r < \sigma,$$
$$\chi = 0 \quad \text{for} \quad r > \sigma,$$
$$g(r, \mathrm{T}) = 0 \quad \text{for} \quad r > 2\sigma.$$

Therefore

$$\Phi_2(\mathrm{T}) = 2\pi\mathrm{N}^2\int_\sigma^{2\sigma} r^2 g(r, \mathrm{T})\,dr.$$

It may be easily shown that for values of r between σ and 2σ

$$g(r, \mathrm{T}) = -\frac{\pi}{3}\left(4\sigma^3 - 3\sigma^2 r + \frac{r^3}{4}\right).$$

Therefore

$$\Phi_2(T) = -\tfrac{17}{36}\pi^2 N^2 \sigma^6.$$

Also

$$\Phi_1(T) = \tfrac{4}{3}\pi N \sigma^3.$$

Writing as usual $\tfrac{2}{3}\pi N \sigma^3 = b$, this gives

$$\Phi_1(T) = 2b, \qquad \Phi_2(T) = -\tfrac{17}{16}b.$$

Substituting these values in equation (e) we obtain

$$pv = RT + RT\frac{b}{v} + \frac{5}{8}RT\left(\frac{b}{v}\right)^2.$$

Molecules of a General Type.

By an extension of this method the virial of a gas consisting of molecules of a very general type may be found.

In each of the identical molecules we choose a point C as centre, and an axis, " l," passing through C ; also a plane " s " containing the axis. These elements are similarly situated in all the molecules. Also let O be a fixed point in space, L a fixed direction, and S a plane containing L. Then the situation of the centre of a molecule is given by " r," the length OC ; θ_1, the angle between OC and L, that is the co-latitude of C : and ϕ the longitude of C measured from the plane S. The element of volume is then

$$dv = r^2 \sin \theta_1 \, d\theta_1 \, d\phi \, dr.$$

The orientation of a molecule is given by θ_2, the angle between the axis l and the direction L ; ψ_1 the angle between the plane S and the plane L, l ; ψ_2 the angle between the plane s and the plane L, l.

As before, suppose that there are $\nu + 1$ molecules in a vessel of unit volume. Then instants are chosen, without regard to the position of the centre of a certain one of these molecules, but in which the arrangement of the other ν molecules, both as regards the position of their centres and their orientations, is always the same, and in which, at the same time, the orientation of the single molecule is always within certain infinitesimal limits. We may now, as before, write down the probability that the centre of the particular molecule is in a given element of volume, dv, in one of these instants. For, as already stated, this probability is equal to

$$B e^{-\chi/kT} dv. \quad \ldots \quad \ldots \quad (f)$$

In this expression χ is the work required to bring the centre of the molecule, orientated in the particular way, from a region outside the influence of any other molecule into the particular volume element dv. χ is some definite function of the quantities ϕ, θ_1, θ_2, ψ_1, ψ_2, r. B is a quantity, independent of the position of C, which is determined as follows.

When the single molecule is outside the influence of any other molecule the probability that θ_2 lies between the values θ_2 and $\theta_2 + d\theta_2$ is $\frac{1}{2}\sin\theta_2\,d\theta_2$. The probability that ψ_1 is between ψ_1 and $\psi_1 + d\psi_1$ is $\frac{1}{2\pi}d\psi_1$: and the probability that ψ_2 is between ψ_2 and $\psi_2 + d\psi_2$ is $\frac{1}{2\pi}d\psi_2$. Therefore the probability that the molecule is simultaneously orientated between these limits is

$$\frac{1}{8\pi^2}\sin\theta_2\,d\psi_1\,d\psi_2\,d\theta_2.$$

This may be written $d\omega$ for short. If P_0 is the " concentration" of this molecule in free space, then the probability that it is orientated in the above way, and that, simultaneously, its centre is in a particular element dv of free space, is therefore $P_0\,d\omega\,dv$. Comparing this with (f), in which χ is made equal to 0, we see that $B = P_0\,d\omega$. Therefore the probability that the molecule is orientated and situated within the given limits is

$$P_0\,e^{-\chi/kT}d\omega\,dv.$$

The value of P_0 is found, exactly as in the case of spherically symmetrical molecules, as follows.

Since the above probability refers to a single molecule, therefore

$$P_0\int e^{-\chi/kT}d\omega\,dv = 1,$$

the integration being taken over all orientations and the whole volume of the vessel. Since the vessel is of unit volume and large compared with the field of a molecule,

$$P_0 = \frac{1}{1 - f(\nu,\,T)},$$

in which

$$f(\nu,\,T) = \int(1 - e^{-\chi/kT})\,d\omega\,dv.$$

The activity, A, is given by

$$A = \frac{C}{1 - f(\nu,\, T)}.$$

Also as before,

$$dp/C = RT\, d\log A.$$

When the gas is not too concentrated, so that we may neglect triple encounters, then

$$f(\nu,\, T) = \nu\phi(T),$$

$\phi(T)$ being the value of the above integral taken, not throughout the whole volume of the vessel, but over the whole field of a single molecule.

The integral involves the relative positions of two molecules. We may consider one molecule to be fixed with its centre C_1 in the point of origin O, and with its axis l_1 and reference plane s_1 to coincide with the fixed direction L and plane S. Then r is the distance C_1C_2 between the centres of the two molecules; θ_1 is the angle between C_1C_2 and the axis l_1; ϕ is the angle which the plane containing l_1 and C_1C_2 makes with the plane s_1. Also θ_2 is the angle between the two axes l_1 and l_2; ψ_1 and ψ_2 the angles between the plane of the two axes and the planes s_1 and s_2 respectively.

Then

$$\phi(T) = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} \int_0^{2\pi} \int_0^{\infty} (1 - e^{-\chi/kT})\, r^2$$
$$\sin\theta_1 \sin\theta_2\, d\psi_1\, d\psi_2\, d\theta_1\, d\theta_2\, d\phi\, dr.$$

Without altering the form of the above expression it is possible to alter the meaning of some of the symbols so that the two molecules are involved symmetrically. As before, r is the distance C_1C_2 between the two centres. θ_1 and θ_2 are the angles which the axes l_1 and l_2 make with the line of centres; ϕ the angle between the two planes l_1, C_1C_2 and l_2, C_1C_2, that is between the two planes which contain the line of centres and the two axes; and ψ_1 and ψ_2 the angles which the planes s_1 and s_2 make with the planes l_1, C_1C_2 and l_2, C_1C_2 respectively.

If now we write $N\phi(T) = \Phi(T)$ we obtain, exactly as in the case of molecules of spherical symmetry,

$$pv = RT + \frac{RT\, \Phi(T)}{2v}.$$

The working out of any actual case will usually be complicated. It will be sufficient here to give the result [*] when the gas consists of hard spherical molecules at the centre of each of which is an electric doublet of constant moment. In this case the potential function χ will not contain the angles ψ_1 and ψ_2. If σ is the diameter of the molecules, and if χ_σ is the work required to separate to infinity two molecules placed in contact with the axes of the doublets parallel and at right angles to the line of centres, then writing $\frac{2}{3}\pi N\sigma^3 = b$,

$$pv = RT + \frac{RTb}{v} - \frac{RTb}{v}\left\{\frac{1}{3}\left(\frac{\chi_\sigma}{kT}\right)^2 + \frac{1}{75}\left(\frac{\chi_\sigma}{kT}\right)^4 + \frac{29}{55125}\left(\frac{\chi_\sigma}{kT}\right)^6 + \dots\right\}.$$

It will be noticed that the virial term independent of T is absent. At sufficiently high temperatures the relation approximates to

$$pv = RT + \frac{RTb}{v} - \frac{N^2 b \chi_\sigma^2}{3RTv}.$$

Thus the attraction virial tends to disappear as the temperature is raised. The explanation of this is indicated as follows.

The potential of a molecule in the field of another is exactly reversed in sign by turning its axis through two right angles. At high temperatures there are very nearly equal numbers of pairs of molecules orientated in the two kind of ways, so that the two sets neutralize each other's effect on the attraction virial. When there is no such balancing effect the virial term independent of T will exist.

The Second Virial Coefficient of a Binary Mixture of Gases.

It is impossible to calculate the virial coefficient B for a mixture of two gases from the values of the coefficients B_1 and B_2 of the separate gases. The interaction of the two unlike molecules introduces a new factor.

Suppose that there are ν_1 molecules of the gas 1 and ν_2 molecules of the gas 2 in a vessel of unit volume. Let ν_{0_1} and ν_{0_2} be the concentrations of molecules of gas 1 and 2 respectively outside the field of any other molecule. Then it is evident from the previous deductions that

$$\nu_{0_1} = \frac{\nu_1}{1 - f_1(\nu_1, \nu_2, T)}, \qquad \nu_{0_2} = \frac{\nu_2}{1 - f_2(\nu_1, \nu_2, T)}.$$

[*] Keesom, *loc. cit.* p. 271.

In these expressions

$$f_1(\nu_1, \nu_2, T) = \int (1 - e^{-\chi_1/kT}) \, d\omega \, dv,$$

$$f_2(\nu_1, \nu_2, T) = \int (1 - e^{-\chi_2/kT}) \, d\omega \, dv,$$

the integrations being taken for all positions and orientations of a molecule of gas 1 and 2 respectively over all the fields due to the other molecules in their actual positions at any given instant. χ_1 and χ_2 are the potentials of the molecule of gas 1 and of gas 2 in the instantaneous field due to the other molecules.

If C is the total gram molecular concentration of the mixture, and n_1 and n_2 are the molecular fractions of the two gases, then the quantities

$$A_1 = \frac{n_1 C}{1 - f_1(\nu_1, \nu_2, T)}, \qquad A_2 = \frac{n_2 C}{1 - f_2(\nu_1, \nu_2, T)},$$

are the activities of the two gases in the mixture. It may be readily shown that

$$dp/C = RT n_1 \, d\log A_1 + RT n_2 \, d\log A_2. \quad . \quad . \quad (g)$$

If the simultaneous approach of three or more molecules be neglected, then

$$f_1(\nu_1, \nu_2, T) = \nu_1 \phi_1(T) + \nu_2 \phi_{12}(T),$$

$$f_2(\nu_1, \nu_2, T) = \nu_2 \phi_2(T) + \nu_1 \phi_{21}(T).$$

In these expressions

$$\phi_1(T) = \int (1 - e^{-\chi/kT}) \, d\omega \, dv,$$

the integration being taken for all positions and orientations of a molecule of gas 1 over the entire field of a molecule of gas 1 ; $\phi_2(T)$ is the corresponding quantity for a molecule of gas 2 in the field of a molecule of gas 2 : and $\phi_{12}(T)$ for a molecule of gas 1 in the field of a molecule of gas 2. It is evident that $\phi_{12}(T) = \phi_{21}(T)$. Thus

$$A_1 = \frac{n_1 C}{1 - C\{n_1\Phi_1(T) + n_2\Phi_{12}(T)\}},$$

$$A_2 = \frac{n_2 C}{1 - C\{n_2\Phi_2(T) + n_1\Phi_{12}(T)\}}.$$

If these values be substituted in (a) we obtain to the required
degree of approximation

$$pv = \text{RT} + \text{RT}\left\{ \frac{n_1{}^2\Phi_1(\text{T}) + 2n_1n_2\Phi_{12}(\text{T}) + n_2{}^2\Phi_2(\text{T})}{2v} \right\},$$

in which v is written for $1/\text{C}$.

As a corollary of this it follows that for gases that are not
too concentrated, so that the third virial coefficient may be
neglected, if n_1 gram molecules of a gas 1 occupying a
volume v exert a pressure p_1 : and if n_2 gram molecules of
a gas 2 occupying the same volume exert a pressure p_2 ;
then when both these quantities of gas together occupy the
volume v they will exert a pressure equal to $p_1 + p_2 + \Delta p$,
where

$$\Delta p = \text{RT}\,\frac{n_1n_2\Phi_{12}(\text{T})}{v^2}.$$

Such experiments as have been performed on the volume
pressure relation of binary mixtures have mostly been carried
out at high pressures. While such experiments may afford
valuable qualitative evidence, yet any deduction from them
of an exact nature concerning the interaction between the
unlike molecules is very difficult.

It is sometimes considered advantageous to use high con-
centrations, because it is supposed that thereby the molecules
are made to approach each other more nearly and so produce
forces which otherwise would not be exerted. So long, how-
ever, as the temperature is not raised the molecules do not
approach each other more nearly but only more frequently.
Therefore, although the effect to be measured is larger,
nothing essentially new is obtained by the use of higher
pressures, except the influence of multiple encounters, which
from the present point of view should be looked upon as a
disadvantageous complication.

On the other hand, careful differential measurements made
at moderate pressures have the great advantage of yielding
to the simple mathematical treatment given above. In order
to deduce the real nature of the interaction it is necessary
that measurements be made not only at one temperature but
at several over a fairly wide range. If this were done in-
teresting results as to the " collision volume " of, for example,
a monatomic molecule and a complex one could be deduced,
and also something concerning the forces between them.

Chemical Department,
The University, Manchester,
    May 1923.

XXVII. *On the Lateral Vibrations of Rods of Variable Cross-section. By* DOROTHY M. WRINCH, *D.Sc., Fellow of Girton College, Cambridge, and Member of the Research Staff, University College, London* *.

IN a preceding paper †, the lateral vibrations of a thin conical bar with a free tip and various conditions of support at its base were discussed, mainly from the point of view of the nodal arrangement associated with the various tones. The object of the present paper is to extend this investigation to thin bars of certain other very general types.

If a bar has a cross-section of area ω at a distance w from its tip, and if the section has a radius of gyration k about a central axis in its plane perpendicular to the lateral displacement, the equation of motion is known to be ‡

$$\frac{\partial^2}{\partial w^2}\, E\omega k^2\, \frac{\partial^2 y}{\partial w^2} + \omega\rho\, \frac{\partial^2 y}{\partial t^2} = 0,$$

where y is the lateral displacement and E, ρ are respectively Young's modulus and the density of the bar, it being assumed that the rotary inertia of the bar § may be neglected. We will assume that a longitudinal section of the bar which cuts any one cross-section in a line which is a principal axis of that section cuts every other cross-section in lines which are principal axes of those sections, and we will discuss only those vibrations in which the displacement is in a direction perpendicular to a set of principal axes of the cross-sections. As we pass from section to section, ω and k both vary and are functions of the distance of the section from the tip of the bar.

The cases of practical interest which arise all appear to be included in the class of problems for which ω and k are proportional to powers of the distance from the tip. If we write

$$\omega = A w^{2\lambda}, \quad k^2 = B w^{2\mu},$$

where A and B are constants, the differential equation becomes

$$\frac{\partial^2}{\partial w^2}\, w^{2\lambda + 2\mu}\, \frac{\partial^2 y}{\partial w^2} = -\frac{\rho}{EB}\, w^{2\lambda}\, \frac{\partial^2 y}{\partial t^2} :$$

on this occasion, for reasons which will appear subsequently, we will consider only those cases in which $\mu < 2$.

* Communicated by the Author.
† Proc. Roy. Soc. A. vol. ci. pp. 493–508 (1922).
‡ Kirchhoff, *Sitz. der Akad. zu Berlin*, 1879, p. 815.
§ Rayleigh, 'Theory of Sound,' vol. i. p. 286.

For a periodic motion, of period $\dfrac{2\pi}{p'}$, the equation becomes

$$\frac{\partial^2}{\partial w^2}\, w^{2\lambda+2\mu}\frac{\partial^2 y}{\partial w^2} = \frac{\rho p'^2}{E\bar{B}}\, w^{2\lambda}y,$$

and the values of p will be determined from this equation together with the conditions at the ends of the bar. If k' be the radius of gyration about another central axis in the cross-sections, the equation of motion when the displacement y is in a direction perpendicular to this axis is

$$\frac{\partial^2}{\partial w^2}\, w^{2\lambda+2\mu'}\frac{\partial^2 y}{\partial w^2} = \frac{\rho p^2}{E B'}\, w^{2\lambda}y, \quad \text{if} \quad k'^2 = B' w^{2\mu'}.$$

and this equation and the conditions at the ends of the bar will give the periods of this set of vibrations. In general, when μ and μ' are not equal, each type of oscillation will possess its own set of periods and its own characteristic nodal arrangement associated with the various periods. It will be sufficient to investigate the characteristics of the vibrations associated with one radius of gyration, say that to which the index μ applies.

As an example of the type of bar to which the analysis is applicable, we may cite the case of a bar which has an elliptic cross-section with axes a and a', such that

$$a = A w^{\mu}, \qquad a' = A' w^{\mu'}.$$

The area of the cross-section at a distance w from the tip will be proportional to $w^{\mu+\mu'}$, and the principal radii of gyration are given by

$$k^2 = \frac{A^2}{4}\, w^{2\mu}, \qquad k'^2 = \frac{A'^2}{4}\, w^{2\mu'},$$

and ω will be proportional to $w^{\mu+\mu'}$. Inserting these values in the general equation, we shall obtain the two equations of motion.

The Characteristic Equation of Motion.

If we introduce a new variable z, defined by the relations

$$z = qw, \qquad q^{4-2\mu} = \frac{\rho p^2}{E\bar{B}},$$

the equation of motion becomes

$$\frac{\partial^2}{\partial z^2}\, z^{2\lambda+2\mu}\frac{\partial^2 y}{\partial z^2} = z^{2\lambda}y.$$

With the use of the operator

$$\vartheta_z = z\frac{\partial}{\partial z},$$

we may write the equation in the form

$$\vartheta(\vartheta-1)z^{2\lambda+2\mu-2}\vartheta(\vartheta-1)y = z^{2\lambda+2}y.$$

or

$$(\vartheta+2\lambda+2\mu-2)(\vartheta+2\lambda+2\mu-3)\vartheta(\vartheta-1)y = z^{4-2\mu}y.$$

It will evidently be convenient to make the substitutions

$$s = \frac{2}{2-\mu}, \qquad x = sz^{1/s}, \qquad \vartheta_x = s\vartheta_z,$$

for the equation then becomes

$$\vartheta(\vartheta+4a_1)(\vartheta+4a_2)(\vartheta+4a_3)y = x^4y,$$

where

$$4a_1, \ 4a_2, \ 4a_3 = -s, \ s(2\lambda+2\mu-2), \ s(2\lambda+2\mu-3).$$

This equation is the *characteristic equation* in its most convenient form. Since we are considering only those cases in which $\mu < 2$, s is positive, and the tip of the bar is therefore given by

$$z = x = 0.$$

We will take the bar to be of unit length. Then the base is given by

$$z = q, \qquad x = sq^{1/s}.$$

Series Solutions of the Characteristic Equation.

There are, in general, four series solutions of the characteristic equation. They are series of hypergeometric type with four denominators [*]. The general form for the displacement is, in fact, in general

$$\mathbf{y} = Ay + A_1y_1 + A_2y_2 + A_3y_3,$$

where A, A_1, A_2, A_3 are constants determined by the conditions of support, and

$$y = F(x^4/4^4 ; a_1, a_2, a_3)$$
$$= 1 + \frac{(x/4)^4}{1!(1+a_1)(1+a_2)(1+a_3)}$$
$$+ \frac{(x/4)^8}{2!(1+a_1)(2+a_1)(1+a_2)(2+a_2)(1+a_3)(2+a_3)} + \dots$$

$$y_1 = x^{-4a_1}F(x^4/4^4 ; \ -a_1, a_2-a_1, a_3-a_1),$$
$$y_2 = x^{-4a_2}F(x^4/4^4 ; \ -a_2, a_3-a_2, a_1-a_2),$$
$$y_3 = x^{-4a_3}F(x^4/4^4 ; \ -a_3, a_1-a_3, a_2-a_3).$$

* *Cp.* Phil. Mag. vol. xlv. pp. 818–827 (1923).

In the present investigation we are concerned only with the case of a bar vibrating with its tip free. In all cases, therefore, the expression for the displacement must be such as to ensure that the shearing stress and bending moment vanish at $x = 0$. These are proportional respectively to

$$z^{2\lambda+2\mu} \frac{\partial^2 y}{\partial z^2}, \qquad \frac{\partial}{\partial z} z^{2\lambda+2\mu} \frac{\partial^2 y}{\partial z^2}.$$

Now, the terms making up the bending moment begin with multiples of z^a, where for y, y_1, y_2, y_3 respectively α is given by

$$2\lambda + 2\mu - 3, \quad 2\lambda + 2\mu - 3 - 4a_1/s, \quad 2\lambda + 2\mu - 3 - 4a_2/s,$$

Since

$$2\lambda + 2\mu - 3 - 4a_3/s.$$

$$4a_1/s = -1, \quad 4a_2/s = 2\lambda + 2\mu - 2, \quad 4a_3/s = 2\lambda + 2\mu - 3,$$

these powers of z are, respectively,

$$2\lambda + 2\mu - 3, \quad 2\lambda + 2\mu - 2, \quad -1, 0.$$

In order that the shearing stress and bending moment may vanish at $x = z = 0$, it is necessary that α should be positive in each case. For y_2 and y_3, α has the values -1 and 0 respectively. Therefore the expression for the displacement cannot contain the series y_2 and y_3. Thus the displacement takes the form

$$\mathbf{y} = \mathrm{A}y + \mathrm{A}_1 y_1.$$

The Rod with clamped base.

If the base of the rod is clamped, the equations

$$\mathbf{y} = \mathrm{A}y + \mathrm{A}_1 y_1 = 0,$$

$$d\mathbf{y}/dz = \mathrm{A}\, dy/dz + \mathrm{A}_1\, dy_1/dz = 0$$

must be satisfied at the point

$$z = q, \quad x = s q^{1/s}.$$

If, therefore, u, a function of x be defined by the relation

$$u = y\, \partial y_1/\partial z - y_1\, \partial y/\partial z,$$

in view of the fact that

$$p = \sqrt{\frac{\mathrm{E}\bar{\mathrm{B}}}{\rho}}\, q^{2/s},$$

the periods associated with the first, second, third, ... rth tones are given by

$$\frac{2\pi}{p} = 2\pi\sqrt{\frac{\rho}{\mathrm{EB}}} \cdot \left(\frac{b_r}{s}\right)^{-2},$$

where $b_1, b_2, \ldots b_r, \ldots$ are the roots in order of magnitude of the equation

$$u(x) = 0.$$

We proceed to find the linear differential equation satisfied by the function $u(x)$.

Writing $\mathrm{P} = y_1$, $\mathrm{Q} = y$, we have

$$u = \frac{d\mathrm{P}}{dz}\mathrm{Q} - \frac{d\mathrm{Q}}{dz}\mathrm{P} = \mathrm{P'Q} - \mathrm{Q'P},$$

and P and Q are two solutions of the equation

$$\frac{\partial^2}{\partial z^2} z^{2m} \frac{\partial^2 y}{\partial z^2} = z^{2\lambda}y \qquad (m = \lambda + \mu),$$

which may also be written

$$z^4 y^{\mathrm{iv}} + 4mz^3 y^{\mathrm{iii}} + 2m(2m-1)z^2 y^{\mathrm{ii}} = z^{4/s}y. \quad . \quad . \quad (1)$$

It will be convenient to introduce the notation, after Nicholson[*],

$$\mathrm{P}_s\mathrm{Q}_r = \frac{d^r\mathrm{Q}}{dz^r} \cdot \frac{d^s\mathrm{P}}{dz^s} - \frac{d^r\mathrm{P}}{dz^r} \cdot \frac{d^s\mathrm{Q}}{dz^s}.$$

Then

$$\mathrm{P}_1\mathrm{Q} = u \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$z^4\mathrm{P}_4\mathrm{Q} + 4mz^3\mathrm{P}_3\mathrm{Q} + 2m(2m-1)z^2\mathrm{P}_2\mathrm{Q} = 0, \quad . \quad . \quad (3)$$

$$z^4\mathrm{P}_4\mathrm{Q}_1 + 4mz^3\mathrm{P}_3\mathrm{Q}_1 + 2m(2m-1)z^2\mathrm{P}_2\mathrm{Q}_1 = z^{4/s}\mu, \quad (4)$$

$$z^4\mathrm{P}_4\mathrm{Q}_2 + 4mz^3\mathrm{P}_3\mathrm{Q}_2 = z^{4/s}\mathrm{P}\mathrm{Q}_2, \quad . \quad . \quad . \quad . \quad (5)$$

and evidently

$$\mathrm{P}_r\mathrm{Q}_r = 0.$$

Differentiating the equation (2) three times, we find

$$\mathrm{P}_2\mathrm{Q} = \frac{1}{z}\vartheta u, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\mathrm{P}_3\mathrm{Q} + \mathrm{P}_2\mathrm{Q}_1 = \frac{1}{z^2}\vartheta(\vartheta-1)u, \quad . \quad . \quad . \quad (7)$$

$$\mathrm{P}_4\mathrm{Q} + 2\mathrm{P}_3\mathrm{Q}_1 = \frac{1}{z^3}\vartheta(\vartheta-1)(\vartheta-2)u. \quad . \quad . \quad (8)$$

[*] Proc. Roy. Soc. A. vol. xcvi. p. 506 (1917).

Eliminating P_4Q by means of the equations (3) and (8), we have

$$2P_3Q_1 - \frac{4m}{z} P_3Q = \frac{1}{z^3} \vartheta \{(\vartheta-1)(\vartheta-2) + 2m(2m-1)\} u,$$

and eliminating P_3Q by means of (7) we obtain

$$2P_3Q_1 + \frac{4m}{z} P_2Q_1 = \frac{1}{z^3} \vartheta \{(\vartheta-1)(\vartheta-2) + 4m(\vartheta-1) + 2m(2m-1)\} u$$

$$= \frac{1}{z^3} \vartheta(\vartheta+2m-1)(\vartheta+2m-2)u. \quad . \quad (9)$$

Differentiating (9) we find that

$$2P_4Q_1 + 2P_3Q_1 - \frac{4m}{z^2} P_2Q_1 + \frac{4m}{z} P_3Q_1$$

$$= \frac{1}{z^4} \vartheta(\vartheta-3)(\vartheta+2m-1)(\vartheta+2m-2)u,$$

and this result combined with the equation (4) becomes

$$2z^4P_3Q_2 - 4mz^3P_3Q_1 - 8m^2z^2P_2Q_1$$

$$= \vartheta(\vartheta-3)(\vartheta+2m-1)(\vartheta+2m-2)u + 2z^{4/s}u.$$

Taken in conjunction with (9) it may be written

$$2z^4P_3Q_2 = \{\vartheta(\vartheta+2m-1)(\vartheta+2m-2)(\vartheta+2m-3) + 2z^{4s}\} u.$$
$$\quad . \quad . \quad (10)$$

A further differentiation yields the result

$$2P_4Q_2 = \frac{1}{z^5} \{\vartheta(\vartheta-4)(\vartheta+2m-2)\}u.$$

If we combine this equation with the equation (10) the result is

$$(\vartheta+2m-1)(\vartheta+2m-2)(\vartheta+2m-3)(\vartheta+4m-4)u + 4z^{4/s}(\vartheta+m+\lambda)u = 0, \quad (11)$$

a linear differential equation of the fifth order for the function $u(x)$.

To obtain the solution of this equation, we may consider the equation

$$\vartheta(\vartheta+\alpha_1)(\vartheta+\alpha_2)(\vartheta+\alpha_3)(\vartheta+\alpha_4)y = z(\vartheta+1+\alpha)y. \quad (12)$$

One solution is evidently

$$y = \mathrm{F}(z\,;\,\alpha\,;\,\alpha_1,\,\alpha_2,\,\alpha_3,\,\alpha_4)$$

$$= 1 + \frac{(1+\alpha)z}{1\,!\,(1+\alpha_1)(1+\alpha_2)(1+\alpha_3)(1+\alpha_4)} + \cdots.$$

Next, if we write

$$y = z^{-\alpha_1}\mathrm{Y}, \qquad \vartheta y = z^{-\alpha_1}(\vartheta - \alpha_1)\mathrm{Y},$$

the equation for Y is

$$(\vartheta - \alpha_1)\vartheta(\vartheta + \alpha_2 - \alpha_1)(\vartheta + \alpha_3 - \alpha_1)\mathrm{Y} = z(\vartheta + 1 + \alpha - \alpha_1)\mathrm{Y},$$

and one solution is evidently

$$\mathrm{Y} = \mathrm{F}(z\,;\,\alpha - \alpha_1\,;\,\alpha_2 - \alpha_1,\,\alpha_3 - \alpha_1,\,\alpha_4 - \alpha_1,\,-\alpha_1).$$

Therefore, another solution of the equation for y is

$$y_1 = z^{-\alpha_1}\mathrm{F}(z\,;\,\alpha - \alpha_1\,;\,\alpha_2 - \alpha_1,\,\alpha_3 - \alpha_1,\,\alpha_4 - \alpha_1,\,-\alpha_1).$$

The symmetry of the equation in α_1, α_2, and α_3 at once shows that the remaining solutions are

$$y_2 = z^{-\alpha_2}\mathrm{F}(z\,;\,\alpha - \alpha_2\,;\,\alpha_3 - \alpha_2,\,\alpha_4 - \alpha_2,\,\alpha_1 - \alpha_2,\,-\alpha_2),$$

$$y_3 = z^{-\alpha_3}\mathrm{F}(z\,;\,\alpha - \alpha_3\,;\,\alpha_4 - \alpha_3,\,\alpha_1 - \alpha_3,\,\alpha_2 - \alpha_3,\,-\alpha_3),$$

$$y_4 = z^{-\alpha_4}\mathrm{F}(z\,;\,\alpha - \alpha_4\,;\,\alpha_1 - \alpha_4,\,\alpha_2 - \alpha_4,\,\alpha_3 - \alpha_4,\,-\alpha_4).$$

If we write

$$x = kz^{4/s}, \qquad k = 4\left(\frac{s}{4}\right)^4,$$

the period equation will become

$$\vartheta_x(\vartheta_x + \alpha_1)(\vartheta_x + \alpha_2)(\vartheta_x + \alpha_3)(\vartheta_x + \alpha_4)y = -x(\vartheta_x + 1 + \alpha)y,$$

where

$$\alpha_1,\,\alpha_2,\,\alpha_3,\,\alpha_4\,;\,\alpha = \frac{s}{4}(2m-1),\,\frac{s}{4}(2m-2),\,\frac{s}{4}(2m-3),$$

$$\frac{s}{4}(4m-4)\,;\,\frac{s}{4}(m+\lambda)-1$$

$$= k + \frac{s}{4},\,k,\,k - \frac{s}{4},\,2k,\,k - \tfrac{1}{2},$$

with

$$k = \frac{s}{4}(m-1).$$

The series solutions of the period equation are therefore

of hypergeometric type with five denominators and one numerator and may be written in the form

$$y = z^\beta \mathrm{F}\left(-4\left(\frac{sz^{1/s}}{4}\right)^4 ; c ; d_1, d_2, d_3, d_4\right),$$

with various values of the parameters β, c, d_1, d_2, d_3, d_4. Of these various solutions one is proportional to the function $u(x)$. To discover which solution it is which has this property, we remark that the function u begins with a term independent of z. Hence, the function u will be a multiple of the series in which $\beta = 0$. This is evidently the series

$$\mathrm{F}\left(-4\left(\frac{sz^{1/s}}{4}\right)^4 ; \alpha ; \alpha_1, \alpha_2, \alpha_3, \alpha_4\right).$$

The period equation therefore takes the form

$$\mathrm{F}\left(-4\left(\frac{x}{4}\right)^4 ; \alpha ; \alpha_1, \alpha_2, \alpha_3, \alpha_4\right) = 0, \quad . \quad . \quad (13)$$

and the periods are given by

$$\frac{2\pi}{p} = 2\pi \sqrt{\frac{\rho}{\mathrm{BE}}} \left(\frac{b_r}{s}\right)^{-2},$$

where $b_1, b_2, b_3 \ldots b_r \ldots$ are the roots of this equation in order of magnitude.

The Roots of the Period Equation for the Rod with clamped base.

The roots of the equation (13) may be found by means of the asymptotic expansion of the hypergeometric function in question. The numerical discussion for special values of the parameters of the successive roots, which alone has been attempted by previous writers, throws no light on the general characteristics of the roots. Employing the asymptotic expansion [*], we obtain an approximation to the roots in the form

$$b_r = \gamma_r + \frac{\nu_1}{2\gamma_r}$$

if

$$\gamma_r = \frac{\pi}{4}\sigma + (r - \tfrac{1}{2})\pi,$$

$$\sigma = \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 - \alpha + 3,2,$$

the terms of order $1/\gamma_r^2$ being neglected.

* *Cp.* a paper by the present writer, Phil. Mag. vol. xlv. pp. 818–827 (1923).

In this expression,

$$\nu_1 = \tfrac{1}{4}(\Sigma_2 + 6\Sigma_1 + 25),$$

where Σ_n denotes the sum of the products n at a time of the five quantities

$$-\sigma, \quad 4\alpha_1 - \sigma, \quad 4\alpha_2 - \sigma, \quad 4\alpha_3 - \sigma, \quad 4\alpha_4 - \sigma.$$

Since

$$\alpha_1, \alpha_2, \alpha_3, \alpha_4 = k \pm \frac{s}{2}, \ k, \ 2k,$$

the five quantities involved are

$$-4k - 2, \quad s - 2, \quad -2, \quad -s - 2, \quad 4k - 2,$$

and we deduce at once that $\Sigma_1 = -10$, and owing to the symmetric nature of the values of the parameters,

$$\Sigma_2 = -(4k+2)(4k-2) - (s-2)(s+2) + 32$$
$$= 40 - 16k^2 - s^2.$$

Therefore

$$\nu_1 = \tfrac{1}{4}(5 - 16k^2 - s^2),$$

$$\gamma_r = \pi(k + r),$$

and the approximation takes the convenient form

$$b_r = \gamma_r + \tfrac{1}{4}(5 - 16k^2 - s^2) / 2\gamma_r$$

if terms of order $1/\gamma_r^2$ are neglected. Thus the periods for the free-clamped bar are given by

$$\frac{2\pi}{l'} = 2\pi \sqrt{\left(\frac{\rho}{BE}\right)} s^2 (\gamma_r + (5 - 16k^2 - s^2) / 8\gamma_r)^{-2},$$

terms of order $1/\gamma_r^2$ being neglected. The periods are therefore expressed in terms of two parameters, which may be called indices for the bar. Now the bar was specified by the conditions

$$\omega = A w^{2\lambda}, \qquad k^2 = B w^{2\mu}$$

and

$$s = 2/(2 - \mu), \quad k = \frac{s}{2}(\lambda + \mu - 1).$$

Evidently, then, the value of A is quite irrelevant to the periods of the bar, whatever the conditions of support. Thus, for example, all conical rods, which have the same indices s, k, will have the same periods if the value of the

constant $\frac{\rho}{BE}$ is the same for all the rods. Further, neither A nor B, nor the particular values of E and ρ for the bar is relevant to the ratios of the periods.

The Nodal Equation.

The displacement at any point of the bar is given by

$$\mathbf{y} = \mathbf{A}y + \mathbf{A}_1 y_1.$$

Owing to the fact that the base of the bar is clamped,

$$0 = \mathbf{A}y + \mathbf{A}_1 y_1,$$

when x has any of the values

$$b_1, \quad b_2, \quad \dots b_r \dots .$$

The nodal equation for the rth tone is therefore

$$\frac{y(x)}{y_1(x)} = \frac{y(b_r)}{y_1(b_r)}.$$

Let

$$_1 b_r, \quad _2 b_r, \quad \dots _m b_r \dots, \quad _r b_r \ (= b_r),$$

be the roots of this equation in order of magnitude. Then the distance of the mth node in the rth tone from the tip (the length of the bar being unity) is given by

$$_m \mathbf{N}_r = (_m b_r)^s.$$

It will be convenient to call these quantities " nodal lengths " and in particular to call $_m \mathbf{N}_r$ " the mth nodal length associated with the rth tone."

The problem of finding the roots of the nodal equation is similar, in some respects, to the problem of finding the roots of the period equation. For, we want to find the whole sequence of roots for which $x < b_r$, and in the rth tone there will, of course, be r of them. Any method which yields the roots one at a time is useless for the purpose of obtaining information about the nodal arrangement which, rather than the accurate determination of a few of the nodal distances associated with the very early tones, is our aim in the present communication. For our purposes, it is plainly more important to use a method which locates the roots of the nodal equation within certain limits than to adopt a procedure which will yield only one root at a time, even if it locates these individual roots to a higher degree of accuracy.

Other Solutions of the Characteristic Equation of Motion.

If we are to investigate the roots of an equation of type

$$\frac{P(x)}{Q(x)} = \frac{P(b)}{Q(b)}$$

by the employment of the asymptotic expansions of the functions, it is evident that it will be desirable that the orders of magnitude of P and Q for large values of x shall be as different as possible. We obtained a nodal equation of this form with

$$P = y_1, \qquad Q = y.$$

But it is evident that we are not limited to this determination of P and Q. We had the equation

$$\mathbf{y} = Ay + A_1 y_1,$$

but this equation might be written in the form

$$\mathbf{y} = CY_1 + DY,$$

where Y and Y_1 are linear combinations of y and y_1, and therefore satisfy the original characteristic equation of motion. The only proviso, namely, that the bending moment and shearing stress shall vanish at the free tip, is evidently satisfied if Y and Y_1 are *any* linear combinations of y and y_1 whatever. Thus we may take a new form for the displacement

$$\mathbf{y} = CY + D_1 Y_1,$$

and the conditions at the base will yield the fact that at $x = b$,

$$CY + D_1 Y_1 = 0,$$

$$C\frac{dY}{dz} + D_1 \frac{dY_1}{dz} = 0.$$

From these equations we can, of course, obtain the period equation in the form

$$Y_1 \frac{dY}{dz} - Y \frac{dY_1}{dz} = 0.$$

This form can be shown to yield the standard form of the period equation given in (13), since Y and Y_1 equally with y and y_1 are solutions of the characteristic equation of motion.

The equations yield the nodal equation in the form

$$\frac{Y(x)}{Y_1(x)} = \frac{Y(b_r)}{Y_1(b_r)},$$

and we proceed now to consider the most advantageous choice of Y and Y_1, not with the view of obtaining convenient convergent expansions for small values of x, but with the express purpose of obtaining functions whose asymptotic behaviour when x is large is convenient for the solution of the equation

$$\frac{Y}{Y_1}(x) = \frac{Y}{Y_1}(b_r). \quad . \quad . \quad . \quad . \quad (14)$$

Now the characteristic equation of motion,

$$\vartheta(\vartheta + 4a_1)(\vartheta + 4a_2)(\vartheta + 4a_3)y = x^4 y,$$

is well known to have four types of asymptotic expansion of its solutions, namely,

$$\mathscr{Y}(a_1,\, a_2,\, a_3) = e^x x^{-\sigma} \left\{ 1 + \frac{\alpha_1}{x} + \ldots \right\},$$

$$\mathscr{Y}_1(a_1, a_2, a_3) = x^{-\sigma} \left\{ \cos\left(x - \frac{\pi\sigma}{2}\right) \right.$$
$$\left. + \frac{\alpha_1}{x} \cos\left(x - \frac{\pi}{2}(\sigma + 1)\right) + \ldots \right\},$$

$$\mathscr{Y}_2(a_1, a_2, a_3) = x^{-\sigma} \left\{ \sin\left(x - \frac{\pi\sigma}{2}\right) \right.$$
$$\left. + \frac{\alpha_1}{x} \sin\left(x - \frac{\pi}{2}(\sigma + 1)\right) + \ldots \right\},$$

$$\mathscr{Y}_3(a_1, a_2, a_3) = e^{-x} x^{-\sigma} \left\{ 1 - \frac{\alpha_1}{x} + \ldots \right\},$$

where

$$\sigma = a_1 + a_2 + a_3 + 3/2 = 4k + 3/2,$$

and $\alpha_1, \alpha_2 \ldots$ are functions of the parameters a_1, a_2, a_3.

With a view to obtaining, in a simple manner, the distribution of roots of the equation (14), it would evidently be most convenient if one of the two functions Y and Y_1 contained in its asymptotic expansion and the other did not contain the series $\mathscr{Y}$, for then the relative order of magnitude of Y and Y_1 would be e^{-x} at most, and an approximation to the roots could quickly be found.

Now, the relation between the solutions y, y_1, y_2, y_3 and the solutions $\mathscr{Y}$, $\mathscr{Y}_1$, $\mathscr{Y}_2$, $\mathscr{Y}_3$ is known. In the first place,

$$\frac{y\,2(2\pi)^{3/2}}{\Gamma(1+a_1)\,\Gamma(1+a_2)\,\Gamma(1+a_3)} = \mathscr{Y}(a_1, a_2, a_3) + \mathscr{Y}_1(a_1\,a_2, a_3),$$

the series $\mathscr{Y}_3$, which is of relative order e^{-x}, being neglected. Since

$$y_1(a_1, a_2, a_3) = x^{-4a_1}y(a_2-a_1, a_3-a_1, -a_1),$$

we have similarly

$$\frac{y_1\,2(2\pi)^{3/2}}{\Gamma(1+a_2-a_1)\,\Gamma(1+a_3-a_1)\,\Gamma(1-a_1)}$$
$$= x^{-4a_1}\left[\mathscr{Y}(a_2-a_1, a_3-a_1, -a_1) + \mathscr{Y}_1(a_2-a_1, a_3-a_1, -a_1)\right],$$

But

$$\mathscr{Y}(a_2-a_1, a_3-a_1, -a_1) = e^z x^{-\tau}\left\{1 + \frac{a_1}{x} + \dots\right\},$$

$$\mathscr{Y}_1(a_2-a_1, a_3-a_1, -a_1)$$
$$= x^{-\tau}\left\{\cos\left(x - \frac{\pi\tau}{2}\right) + \frac{a_1}{x}\cos\left(x - \frac{\pi}{2}(\tau+1)\right) + \dots\right\},$$

where

$$\tau = (a_2 - a_1) + (a_3 - a_1) + (-a_1) + 3/2,$$

just as

$$\sigma = a_1 + a_2 + a_3 + 3/2.$$

Evidently

$$\tau = \sigma - 4a_1.$$

Therefore

$$\frac{y_1\,2(2\pi)^{3/2}}{\Gamma(1+a_2-a_1)\,\Gamma(1+a_3-a_1)\,\Gamma(1-a_1)}$$
$$= \mathscr{Y}(a_1, a_2, a_3) + x^{-\sigma}\left\{\cos\left(x - \frac{\pi}{2}\sigma + 2\pi a_1\right)\right.$$
$$\left. + \frac{a_1}{x}\cos\left(x - \frac{\pi}{2}(\sigma+1) + 2\pi a_1\right) + \dots\right\}.$$

If, therefore, we choose Y to be a multiple of

$$\frac{y_1\,2(2\pi)^{3/2}}{\Gamma(1+a_2-a_1)\,\Gamma(1+a_3-a_1)\,\Gamma(1-a_1)}$$
$$-\frac{y\,2(2\pi)^{3/2}}{\Gamma(1+a_1)\,\Gamma(1+a_2)\,\Gamma(1+a_3)},$$

its asymptotic expansion will contain no series in e^x and will, indeed, be the same multiple of

$$x^{-\sigma}\left\{\cos\left(x-\frac{\pi}{2}\sigma+2\pi a_1\right)+\frac{\alpha_1}{x}\cos\left(x-\frac{\pi}{2}\sigma+\overline{1}+2\pi a_1\right)\ldots\right.$$
$$\left.-\left[\cos\left(x-\frac{\pi\sigma}{2}\right)+\frac{\alpha_1}{x}\cos\left(x-\frac{\pi}{2}\sigma+1\right)+\ldots\right]\right\},$$

which may also be written in the form

$$-2x^{-\sigma}\sin a_1\pi\left\{\sin\left(x-k+\tfrac{3}{4}\pi\right)+\frac{\alpha_1}{x}\sin\left(x-k+\overline{\tfrac{5}{4}}\pi\right)+\ldots\right\},$$

since

$$\sigma/2-\alpha_1=k+3/4.$$

We may conveniently take Y_1 to be equal to

$$\frac{y\,2(2\pi)^{3/2}}{\Gamma(1+a_1)\,\Gamma(1+a_2)\,\Gamma(1+a_3)},$$

for then its asymptotic expansion will be

$$x^{-\sigma}e^x\left\{1+\frac{\alpha_1}{x}+\ldots\right\},$$

terms of relative order e^{-x} being neglected.

The nodal equation associated with the rth tone therefore appears in the form

$$e^{-x}\left\{\sin\left(x-\overline{k+\tfrac{3}{4}}\pi\right)+\frac{\alpha_1}{x}\sin\left(x-\overline{k+\tfrac{5}{4}}\pi\right)+\ldots\right\}\Big/\left(1+\frac{\alpha_1}{x}+\ldots\right)$$
$$=f(x)=f(b_r),$$

where b_r denotes the root of the period equation associated with the rth tone. We have already obtained the value of b_r in the case when the base of the bar is clamped, in the form

$$b_r=\pi(r+k)+\frac{1}{8}\frac{5-16k^2-s^2}{\pi(k+r)}+\ldots.$$

For any other conditions of support at the base the nodal equation for the rth tone still takes the form

$$f(x)=c_r,$$

where c_r is a constant associated with the rth period; the value of c_r for any particular conditions can, of course, be

determined by the formation of a period equation when the conditions at the base have been specified.

To obtain a general idea of the roots of the nodal equation for the bar with clamped base, we put

$$x = (m + k - \tfrac{1}{4})\pi + \epsilon_m,$$

and the equation then becomes

$$e^{-\epsilon_m}\left(\sin \epsilon_m - \frac{2\alpha_1}{(m + k - \tfrac{1}{4})\pi + \epsilon_m} + \dots\right) = f(b_r)e^{(m+k-\tfrac{1}{4})\pi}.$$

Now even in the lower tones, $f(b_r)e^{(m+k-\tfrac{1}{4})\pi}$ is small in order of magnitude. For instance, in the fifth tone, for the first, second, third, and fourth nodes from the tip (for which m takes the values 1, 2, 3, 4, and $r=5$) the order of magnitude of $f(b_r)e^{(m+k-\tfrac{1}{4})\pi}$ is

$$e^{-4\tfrac{1}{4}\pi} = 1 \cdot 59 \times 10^{-6}, \qquad e^{-3\tfrac{1}{4}\pi} = 3 \cdot 68 \times 10^{-5},$$
$$e^{-2\tfrac{1}{4}\pi} = 8 \cdot 51 \times 10^{-4}, \qquad e^{-1\tfrac{1}{4}\pi} = 1 \cdot 97 \times 10^{-2},$$

respectively. Evidently, the higher the node, the more nearly do the roots of the nodal equation approach the roots of the equation

$$f(x) = 0.$$

The solution of the nodal equation associated with any tone can be carried out by successive approximation to any requisite degree of accuracy.

The roots of the equation

$$f(x) = 0$$

can readily be obtained. If ρ_m be the mth root in order of magnitude,

$$\rho_m = \delta_m + \frac{\alpha_1}{\delta_m},$$

with

$$\delta_m = \frac{\pi\sigma}{2} - a_1\pi + (m-1)\pi,$$

terms of order $1/\delta_r^2$ being neglected.

The value of α_1 can easily be obtained owing to the symmetrical nature of the four quantities,

$$-\sigma, \quad 4a_1 - \sigma, \quad 4a_2 - \sigma, \quad 4a_3 - \sigma,$$

which are evidently equal to

$$-2k + \frac{s}{2} - \frac{3}{2}, \quad -2k - \frac{s}{2} - \frac{3}{2}, \quad 2k + \frac{s}{2} - \frac{3}{2}, \quad 2k - \frac{s}{2} - \frac{3}{2}.$$

Thus

$$\Sigma_1 = -6,$$

$$\Sigma_2 = 6\binom{3}{2}^2 - 2\left((2k)^2 + \binom{s}{2}^2\right) = \frac{27}{2} - 8k^2 - \frac{s^2}{2},$$

and, in consequence,

$$\alpha_1 = \tfrac{1}{8}(5 - 16k^2 - s^2),$$

$$\delta_m = \pi(k + m - \tfrac{1}{4}),$$

and ρ_m is given by

$$\rho_m = \pi(k + m - \tfrac{1}{4}) + \frac{5 - 16k^2 - s^2}{8\pi(k + m - \tfrac{1}{4})}.$$

The Nodal Lengths for a free-clamped bar.

Adopting the approximation discussed above, the nodal lengths are given by

$$_mp_r = \left(\frac{\rho_m}{b_r}\right)^s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

with

$$b_r = \pi(k + r) + \frac{5 - 16k^2 - s^2}{8\pi(k + r)},$$

$$\rho_m = \pi(k + m - \tfrac{1}{4}) + \frac{5 - 16k^2 - s^2}{8\pi(k + m - \tfrac{1}{4})}.$$

The first approximation yielded by this result takes the exceedingly simple form

$$_mp_r = \left(\frac{k + m - \tfrac{1}{4}}{k + r}\right)^s,$$

and it is interesting to compare this result, which is in a very convenient shape for practical applications, with results in some particular case which are known to a high degree of accuracy. An obvious case, on which to test our result, is the case of a bar of uniform cross-section vibrating with free tip and clamped base. Seebeck [*] gives the nodal lengths for the rth tone as

($\cdot$3405, 1$\cdot$2455, 2$\cdot$25, 3$\cdot$25, 4$\cdot$25 ...

$$r - 3 + \tfrac{1}{4} - \cdot0044, \quad r - 2 + \tfrac{1}{4} + \cdot0002, \quad r - \tfrac{1}{2}) / (r - \tfrac{1}{2}).$$

* *Abh. Math. Phys. Classe d. k. Sachs. Gesellschaft d. Wissenschaften*, Leipzig, 1852.

Our approximation becomes (since for a uniform bar $\lambda = \mu = 0$, $s = 1$, $k = -\frac{1}{2}$),

$$(\tfrac{1}{4}, 1\tfrac{1}{4}, 2\tfrac{1}{4}, 3\tfrac{1}{4}, 4\tfrac{1}{4}, \ldots r-3+\tfrac{1}{4}, r-2+\tfrac{1}{4}) / (r-\tfrac{1}{2}),$$

and the last term, nominally

$$(r-\tfrac{3}{4}) / (r-\tfrac{1}{2}),$$

must evidently be replaced by unity since the bar is clamped at the base and so has a node there.

The expressions for the nodal ratios associated with a free-clamped bar are independent of the constants (E, ρ, B, A) which are associated with the bar, and depend only on the two indices s and k. This fact throws light upon the results obtained by previous investigators in this field. For, evidently, bars which share the same indices will possess the same characteristic arrangement. A conical bar, for example, whether it has an elliptic cross-section or a rectangular cross-section, will possess the same indices, namely, $s = 1$, $k = 2$. The work of Kirchhoff [*], which ostensibly deals with the case of a conical bar of circular cross-section applies, in fact, so far as the nodal arrangement is concerned, to a wider class of cases.

Certain interesting characteristics of the nodal arrangement in a free-clamped bar may be deduced from the results given in (15). For consider the difference between $_{m+1}p_r$ and $_m p_r$. If we neglect terms in

$$(\pi(k+m-\tfrac{1}{4}))^{-2},$$

this difference is evidently of order

$$(k+r)^{-s}.$$

If, however, we are considering the order of magnitude of this difference, in the case when $r-m$ is small so that it is not permissible to neglect terms of order

$$(\pi(k+m-\tfrac{1}{4}))^{-2},$$

the difference is evidently of order

$$(k+r)^{-1}.$$

Thus, in the case of sufficiently high tones, the nodes near the tip crowd together at intervals of order $(k+r)^{-s}$, whereas the interval between successive nodes is of order $(k+r)^{-1}$. Thus, as s increases the crowding of nodes towards the tip in

* *Loc. cit.*

the higher tones becomes more pronounced.   This result points to the exceptional nature of the case when $s = 0$, which was already evident in the original form of the equation.

Other Conditions of Support at the Base.

Whatever the conditions of support at the base, the fact that the tip of the bar is free involves the consequence that the displacement is given by

$$y = CY + C_1Y_1.$$

The positions of the nodes in the rth tone are therefore determined by the roots of the equation

$$\frac{Y_1}{Y}(x) = c_r.$$

c_r being some constant associated with the rth tone.   This fact is independent of the conditions of support at the base and persists whether the bar is clamped free or supported at its base.   Now an equation of this type will only have r roots if c_r is sufficiently small.   Therefore if we consider a high node, the arguments used in the special case when, in fact, the value of c_r was already known and was indeed given by

$$c_r = \frac{Y_1}{Y}(b_r),$$

apply to the present much wider class of cases, and it is equally satisfactory to adopt the roots of the equation

$$\frac{Y_1}{Y}(x) = 0$$

as approximations to the roots of the equation $\frac{Y_1}{Y}(x) = c_r$.

Thus associated with the rth tone we again have the sequence

$$\rho_1, \rho_2, \ldots \rho_r,$$

defined as before.   The nodal ratios could next be obtained from these quantities, if we had obtained the values of the roots of the period equation associated with the particular conditions of support at the base.   In the general problem of finding characteristics of the nodal arrangement of a bar with free tip, when no specification is given as to the conditions of support at the base, the nodal lengths themselves are not determinate, but, on the other hand, the ratio of the

nodal lengths associated with any one tone can at once be deduced in the form

$$\frac{1p_r}{(\rho_1)^s} = \frac{2p_r}{(\rho_2)^s} \cdots = \frac{mp_r}{(\rho_m)^s} \cdots .$$

In many cases, this fact gives sufficient information for an arrangement of a sequence of values to be recognized as being the nodal arrangement typical of the vibrations of a bar with free tip and particular indices s and k. In particular, in the subset of cases which fall under the general classification of cases in which the tip is free and nothing is known of the conditions of support at the base except that the base is fixed, we can immediately deduce the nodal lengths in the form

$$mp_r = \left(\frac{\rho_m}{\rho_r}\right)^s,$$

for since the bar is at rest at its base there must be a node there.

The general characteristics of the nodal arrangement in the case of a free-clamped bar therefore persist in the case of a bar with free tip and any conditions of support at the base. The nodes still crowd towards the tip, the density of nodes in the neighbourhood of the tip and in the neighbourhood of the base being in the ratio

$$(k+r)^s : (k+r).$$

The above results establish therefore the existence of certain characteristic arrangements of nodes which may be associated with a bar possessing certain indices s and k which is vibrating with a free tip.

XXVIII. *The Crystal Structure of various Heusler Alloys by the Use of X-Rays. By* J. F. T. YOUNG, *M.A.*[*]

[Plate IV.]

I. INTRODUCTION.

AMONG the problems of atomic structure is that of the origin of the magnetic phenomena which are manifest on every side in the diamagnetic, paramagnetic, or ferromagnetic behaviour of all substances. It is of the utmost importance to determine the seat of the magnetic forces and

[*] Communicated by Professor J. C. McLennan, F.R.S.

U 2

the cause of their variation in character in the different elements.

For many years the magnetic properties of substances have been ascribed to the action of molecular magnets, but their nature has never been settled. The early theories of magnetism of Weber, Wiedemann, Ampère, and Maxwell, based on analogies to the phenomena of electromagnetic induction, were more or less artificial and far from satisfactory. The advent of the electron theory of matter provided a new view-point, which Langevin and Wiess extended to provide a theory of magnetism which was in qualitative agreement with experience, at least. In their theory the electrons revolving in certain orbits about the nucleus or centre of the atom created magnetic fields, and each electronic current was equivalent to a definite magnetic moment. When an external magnetic field was supposed, it was shown that these magnetic moments were reduced in the direction of the field, producing the diamagnetic modification of the atom. Paramagnetic properties of atoms were explained by assuming that the resultant magnetic moment of the electronic circuits in such an atom was not zero, and the action of the external field was to rotate these atoms so that their magnetic axes would point in the direction of the field as nearly as the thermal reaction towards disorder would allow. Paramagnetism would thus be a function of the strength of the external field, the resultant magnetic moments of the atoms and the demagnetizing effects of thermal agitation, and any attractive forces between the atoms of any other nature. Weiss extended these conceptions to give a plausible explanation of ferromagnetism by introducing the additional hypothesis that the external field called into action an internal " molecular field " which far exceeded in its effect any other forces on the atom and produced large intensities of magnetization. The later developments by Gans [*] and Frivold [†] of these classical theories, and the applications of the quantum theory by Gans [‡] and Reiche [§] to account for the distribution of energy of rotation of the magneton, all included the hypothesis of an ultimate magnetic unit with a certain magnetic moment, characteristic of the substance, and therefore with a magnetic axis and thus capable of rotation by an external field.

[*] R. Gans, *Ann. d. Phys.* xlix. p. 149 (1916) ; l. p. 163 (1916).
[†] O. E. Frivold, *Ann. d. Phys.* lxv. p. 1 (1921).
[‡] R. Gans, *loc. cit.*
[§] F. Reiche, *Ann. d. Phys.* liv. p. 401 (1917).

At first the magnetic particle was supposed to be the atom or molecule, but other attempts have been made, as in Parson's theory of the magneton, and in other hypotheses regarding the structure of the electron, to give a more definite conception. These have been attended with some success in certain directions. However, the molecular theory of magnetism has given the most coherent explanation of such magnetic effects as (1) the effect of mechanical jarring on magnetism, (2) the influence of chemical combination as in salts and the Heusler alloys, (3) the action of temperature variation, and (4) the general mechanical effects included in the term magnetostriction.

The present work was undertaken with a view of testing these theories in the case of Heusler alloys and of determining what, if any, molecular arrangement was related to magnetic phenomena.

The Heusler alloys, discovered in 1903 [*], were composed of the paramagnetic metals manganese and aluminium and the diamagnetic metal copper in various proportions, and some were found to have ferromagnetic properties comparable with magnetically soft iron. These alloys must then contain the ultimate ferromagnetic particle. It has been shown definitely that the amount of iron impurity present was quite incapable of producing the effects discovered.

There have been several explanations proposed. Guillaume [†] applied Faraday's suggestion that chromium and manganese were non-magnetic at ordinary temperatures because their magnetic transformation temperatures were quite low, and put forward the view that the alloying of manganese with aluminium raised the critical temperature so that in the Heusler alloy the manganese had magnetic properties at ordinary temperatures. There has never been decisive experimental evidence to support this theory, although at various times McTaggart and Robertson [‡], and later Rhead [§], as a result of the micro-photographic study of etched specimens, supposed that the ferromagnetism of the alloys was produced in a special allotropic form of manganese dissolved in copper and aluminium.

Heusler himself [||] built up a theory from the experimental

[*] Fr. Heusler, *Ver. de Phys. Ges.* v. p. 219 (1903).

[†] C. E. Guillaume, *Arch. Sciences Phys. et Nat.* xxiv. p. 381 (1907).

[‡] H. A. McTaggart and Robertson, Proc. Roy. Soc. Can. (3) ii. p. 31 (1908).

[§] E. L. Rhead, Journ. Inst. of Metals, (2) iv. p. 89 (1910).

[||] Fr. Heusler, *Zeits. anorgan. Chemie,* lxi. p. 277 (1909).

bases that copper and aluminium formed an alloy of composition Cu_3Al, and that copper and manganese formed a series of mixed crystals. In his opinion it was possible for the copper of the compound Cu_3Al to be isomorphously replaced by manganese to form complex compounds of the type, $Al_x(MnCu)_{3x}$ or $Al_xCu_aMn_{(3x-a)}$, which he regarded as the carrier of the ferromagnetic properties. Both formulæ were designed to indicate that maximum ferromagnetic properties were associated with alloys in which the copper and manganese atoms together were three times as plentiful as the aluminium atoms. This conception furnished a ready explanation of the fact that freshly cast alloys were not strongly magnetic, but reached their maximum magnetic properties after artificial "ageing," *i.e.* prolonged heat treatment at about 120°C. "Ageing" was represented as the combined action of two simultaneous structural changes, which were identified by a critical study of the variation of magnetic properties with heat treatment. It was shown that either the magnetic moment of the ferromagnetic unit or the number of such units was increased, and at the same time the ability of this unit to rotate freely was more or less reduced. Heusler explained this by saying that at high temperatures the complex compound $Al_xCu_aMn_{(3x-a)}$ was dissociated, but "ageing" gave an opportunity for its formation by association of the constituents. He made the further suggestion that possibly the marked ferromagnetism of the alloys was produced by the individual $Al_xCu_aMn_{(3x-a)}$ molecules which segregated from the solid solution to produce a new crystalline structure.

Various hypotheses have been advanced to explain how ferromagnetic properties could arise in the compound $Al_xCu_aMn_{(3x-a)}$. Richarz [*] thought that new electrons might be set in rotation or their speed and orbital areas changed. Weiss [†] said that probably the magnetons in the manganese atom were much freer to rotate in the alloy than in the elemental state, while Take [‡] ascribed the increased effects with the alloys to an increased magnetic moment per magnetic particle produced by a rearrangement of the electron orbits in the complex molecule. Ross [§], however, took a strong position against any of the above theories of the

* F. Richarz, *Zeits. anorgan. Chemie,* lxi. p. 271 (1909) ; *Physik. Zeits.* xii. p. 155 (1911).
† P. Weiss, *Jl. de Phys.* (4) vi. p. 689 (1907).
‡ E. Take, *Gottinger Abhandl.* viii. No. 2 (1911).
§ A. D. Ross, Trans. Faraday Soc. viii. p. 185 (1912).

Heusler alloys, but believed that the ferromagnetic properties were associated with the occurrence of two intermetallic compounds Cu_3Al and Mn_3Al, the variation in concentration being the cause of variation in the magnetic properties of the alloys. His objection to Heusler's complex compound $Al_xCu_aMn_{3x-a}$, was on the ground that ternary alloys were rare, and a large number of them would be necessary to account for the variation in the quality of the alloys.

In an attempt to distinguish between the above theories and to find some phenomenon which would show a positive variation with magnetic properties, a systematic crystal analysis of definite Heusler alloys in different conditions was undertaken, using X-ray methods.

II. Preparation of the Alloys.

The samples of Heusler alloys used in the present work were the same ones, the magnetic properties of which were investigated some years ago by McLennan and others[*]. They were prepared by melting the constituent metals—copper, manganese, and aluminium, guaranteed chemically pure and free from iron—in a graphite crucible in an ordinary coke furnace, and then casting in moulds. The copper was heated first until it was fluid, and the manganese and aluminium were added in this order to avoid the serious loss of these metals, especially the latter, at high temperatures. A homogeneous alloy was obtained by stirring the molten metals thoroughly with a porcelain rod. The composition of the alloy casting was always very closely given by the amounts of the metals used.

The castings used by the writer were rings which in their final form had the following dimensions: mean radius 3·5 cm., radial thickness 0·6 cm., and width 2·3 cm. Although the alloys were very hard and brittle, it was found possible to machine and grind them to true rings. This not only enabled them to be measured more accurately, but also improved their homogeneity by removing the " skin " of the casting.

The composition of the alloys was known from McLennan's work. The specimens selected for use were :—

Alloy.	Composition.
Alloy IV a ...	15·9 % Al : 23·9 % Mn : 60·3 % Cu.
Alloy III a ...	14·3 % Al : 28·6 % Mn : 57·1 % Cu.

[*] J. C. McLennan, Phys. Rev. 1907.

III. MAGNETIC PROPERTIES OF THE SAMPLES EXAMINED.

The importance of the heat treatment of a Heusler alloy in relation to its magnetic quality has been mentioned already. The history of the "ageing" and other treatment of these alloys by McLennan had been lost in the intervening years, so that with both of them the designation "Condition (1)" shall be taken to mean their magnetic state at the start of this work—*i.e.*, they had been left untouched for fifteen years, during which they had suffered a temperature variation from -10° C. to 45° C., due to climatic changes. Their subsequent treatment and magnetic condition is summarized in the following table :—

TABLE I.—Magnetic Properties of Alloys.

Alloy.	Condition.	Treatment.	Magnetic Condition.
IV a ...	(1)	Heat treatment unknown ; 15 years' natural "ageing."	μ max.$=86.8$ for A $= 7.8$ gauss.
IV a ...	(2)	Heated to a bright red— 600° C. Quenched in cold water.	μ max. $=14.6$ for H $= 8.2$ gauss.
III a ...	(1)	Heat treatment unknown ; 15 years' natural "ageing."	μ max. $= 1.64$ for H $=17.0$ gauss.
III a ...	(2)	Heated to a bright red— 600° C. Quenched in cold water ; then "aged" for 250 hours in an air bath at 110° C.	μ max.$= 2.54$ for H $=18.0$ gauss.

The magnetic properties of these various alloys are illustrated by the graphs of fig. 1 and fig. 2, showing the relation between μ and H.

The magnetic measurements were made in the standard way with a ballistic galvanometer which was calibrated by a Duddell magnetic standard. The primary circuit wound on the rings consisted of either 50 or 100 turns of No. 18 wire and the secondary circuit of 150 turns of No. 22 wire, both circuits being wound uniformly around the ring. A constant speed reversing switch was used in the primary circuit, and the resulting galvanometer deflexion was converted into lines of magnetic induction, B, from the calibration curve. The magnetizing field, H, was determined from the current and dimensions of the primary circuit.

Between each heat treatment the rings were uncovered, and enough filings taken off to provide samples for the crystal analysis.
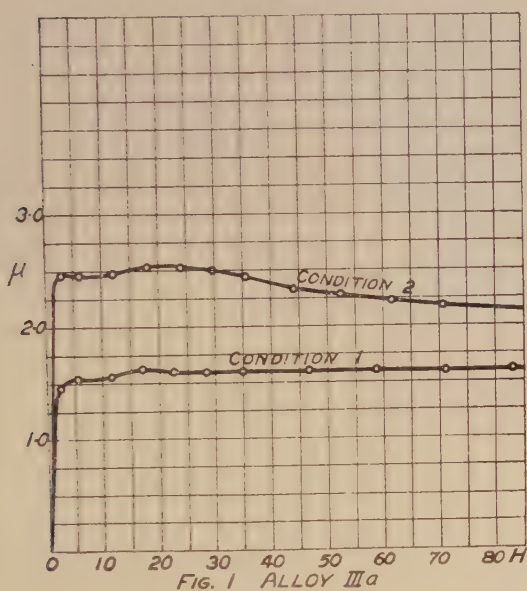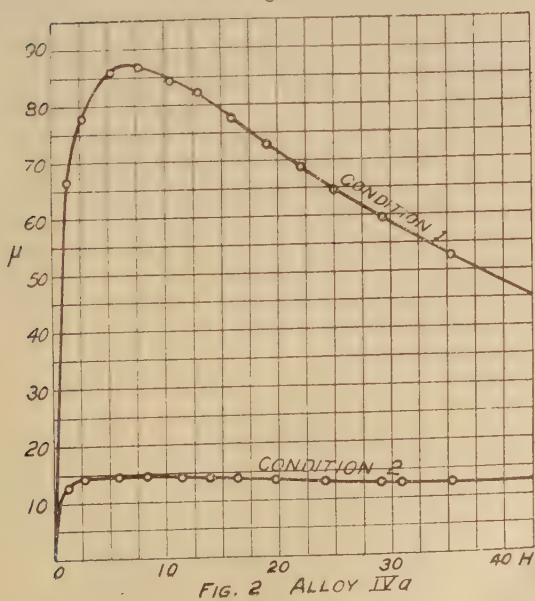
Fig. 1.

FIG. I   ALLOY IIIa

Fig. 2.

FIG. 2   ALLOY IVa

IV. Method of Crystal Analysis.

Since there are no large individual crystals in the Heusler alloys suitable for the Bragg method, the powder method of X-ray analysis was adopted, using a modified form of Hull's arrangement *. The X-ray tube was a Coolidge water-cooled molybdenum target tube, which could be operated continuously at currents up to 30 milliamperes and 30–40 kilovolts potential. A filter, containing 0·05 gm. of ZrO_2 per sq. cm. with collodion as the binder, was used to absorb wave-lengths other than the Kα doublet, 0·712 A.U., for which zirconium has a maximum transparency. The monochromatic X-rays then passed through a slit system of lead in the side of the lead box containing the tube, which confined the beam to a width of 2 mm. The crystal powders of aluminium, manganese, and copper and the Heusler alloys were obtained by filing the metals and sifting them through a 200-mesh gauze. The powder was then mounted in the X-ray beam in a paper cylinder of about 0·6 mm. diameter, which was also at the centre of a semicircular brass frame of 11·25 cm. radius, against which was held a strip of Eastman duplitized X-ray film backed by a calcium tungstate intensifying screen. A brass diaphragm divided the film-holder into two parts, so that the diffraction patterns of two substances could be taken simultaneously by filling one-half of the paper tube with one substance and the other half with another. In this way the unknown pattern could be determined in terms of a selected standard. In the case of the heavy metals—manganese and copper and the alloys—it was found necessary to dilute the crystal powder with corn starch, in order to obtain satisfactory diffraction patterns.

The whole apparatus was arranged so that, in addition to taking the photographs of the alloy powders in their natural state, a horseshoe electromagnet with a narrow gap between the poles could be put in position, and diffraction patterns of the alloys taken when in a magnetic field of 3500 gauss. Iron screens were, of course, used to shield the X-ray tube from the stray magnetic field.

V. Results.

Metallic aluminium was chosen as the standard substance, because it is a constituent of the Heusler alloys ; it gives quite intense reflexions from the various crystal planes, and its crystal form and constants have been evaluated several

* A. W. Hull, Phys. Rev. **x.** (6) p. 661 (1917); xvii. (5) p. 571 (1921).

times by Hull *, Scherrer †. and Kirchner ‡. The pattern obtained by the writer agreed excellently with the previous solutions of the crystal, viz. that aluminium crystallizes in a face-centred cubic system with the lattice constant, $d = 4.05$ A.U. The pattern is shown in No. 1, Pl. IV.

The other constituents of the alloys were then investigated, in order to eliminate any lines which might be due to free metal in the alloy. The comparison method was used throughout the work. The solution of the copper diffraction pattern which is shown in No. 2. Pl. IV., agreed exactly with Bragg's result § from a large crystal, that copper crystallizes in the face-centred cubic system and has a lattice constant, $d = 3.60$ A.U.

The third metal, manganese, presented great difficulties. Although Groth ‖ has placed manganese in the cubic system, the pattern obtained is much too complex for this to seem probable. All attempts to solve the diffraction pattern of manganese by Hull and Davey's graphical method ¶ failed, and although Runge ** and Johnsen & Toeplitz †† have proposed mathematical methods of solution, the power of this analysis has never been tested beyond the simplest cases. In the table are given the values of d/n, calculated from $n\lambda = 2d \sin\theta$ for sixteen of the stronger lines on the manganese pattern shown in No. 3, Pl. IV. There were faint indications of some other lines on some of the films, but they were omitted as probably spurious.

TABLE II.—Manganese Diffraction Pattern.

d/n.	Intensity (estimated).	d/n.	Intensity (estimated).
2·08 A.U.	8	1·23 A.U.	4
1·97	4	1·21	4
1·88	4	1·17	4
1·80	1	1·12	2
1·74	2	1·10	2
1·67	1	1·05	2
1·48	2	0·98	1
1·41	2	0·94	1

* A. W. Hull, Phys. Rev. x. (6) p. 661 (1917).
† P. Scherrer, *Phys. Zeitchr.* xiv. p. 23 (1918).
‡ F. Kirchner, *Ann. d. Phys.* lxix. (17) p. 59 (1922).
§ W. L. Bragg, Phil. Mag. xxviii. p. 335 (1914).
‖ P. Groth, *Elemente der Phys. und Chem. Krystallographie*, 1921.
¶ A. W. Hull and W. P. Davey, Phys. Rev. xvii. (5) p. 549 (1921);
Journ. Opt. Soc. Amer. v. (6) p. 479 (1921).
** C. Runge, *Phys. Zeits.* xviii. p. 509 (1917).
†† A. Johnsen and O. Toeplitz, *Phys Zeits.* xix. p. 47 (1918).

The value of the estimated intensity represents the relative intensity at least, and probably is a measure of the number of co-operating planes for each reflexion.

The photographs of the diffraction patterns of the alloys gave some interesting results, which are summarized in Table III.

TABLE III.—Crystal Structure of Heusler Alloys.

Alloy.	Condition.	μ max.	Remarks.	Crystal Structure.
III *a*......	(1)	1·64	No magnetic field.	Face - centred cube, $d=3\cdot70$ Å.U. (calculated from 5 lines).
III *a*......	(1)	1·64	In a magnetic field of 3500 gauss.	Same as above.
III *a*......	(2)	2·54	No magnetic field.	Same as above.
IV *a*	(1)	86·8	No magnetic field.	Face - centred cube, $d=3\cdot70$ Å.U. (calculated from 5 lines); and, superimposed, a body-centred cube, $d=2\cdot98$ Å.U. (calculated from 3 lines).
IV *a*	(1)	86·8	In a magnetic field of 3500 gauss.	Same as above.
IV *a*......	(2)	14·6	No magnetic field.	Same as above.

Typical patterns of Alloys III *a* and IV *a* are shown in Nos. 4 & 5, Pl. IV.

It will be noted that in no case was there ever any trace on the films of the characteristic lines of any of the free crystalline elements—aluminium, manganese, and copper. This, of course, does not mean that they were completely absent in the alloy. It is unfortunate that the "sensitivity" of the X-ray method to detect the presence of small amounts of foreign crystals in a substance has never been worked out. Andrews [*] mentioned that in the case of a mechanical mixture of zinc and copper powders it was quite easy to detect as low as 10 per cent. zinc, but the lowest limit is unknown. It would no doubt depend on the relative scattering powers of the two metals, but a value which might be proposed tentatively is 5 per cent. The writer hopes to be able to work out this feature of X-ray analysis in the near future.

* Mary R. Andrews, Phys. Rev. xviii. p. 245 (1921).

VI. DISCUSSION.

The fact that there was no evidence of the diffraction patterns of the individual metals—aluminium, manganese, and copper—was considered as indicating that these alloys in the conditions mentioned above were quite homogeneous, and that there had been no very great segregation of the constituents in the solidifying of the castings. A low percentage of the free metals would probably not be detectable. At the same time this would seem to dispose of the allotropic theory proposed first by Guillaume *, and later by McTaggart and Robertson † and by Rhead ‡ in somewhat different forms, for this theory would admit the existence of free aluminium and copper along with a modified form of manganese in proportions which would easily be detected by the X-ray analysis.

The problem is then to find the structure of the Heusler alloy. It is unfortunate in this respect that the crystal structure of manganese is not known. Hull §, from a study of the structure of the ferromagnetic elements, has decided that the property of ferromagnetism does not depend on the arrangement of atoms, but on the distances between them. In the case of many of the elements and some binary alloys containing metals of similar atomic weights, this can be accurately ascertained; but in the case of binary alloys containing an element of low atomic weight and of ternary alloys, the present state of knowledge of X-ray diffraction makes it practically impossible to obtain a complete solution, even if the alloy does yield a perfectly definite diffraction pattern, as in the case of the Heusler alloys.

Ross's ‖ explanation of the magnetic unit in these alloys accounted readily for the variation of magnetic properties, say with heat treatment, as a function of the relative concentrations of the binary alloys Cu_3Al and Mn_3Al. If this be true, there should be, in general at least, two crystal forms, giving diffraction patterns which in any one specimen should vary in relative intensity with change in magnetic permeability. The presence of two crystal lattices in the case of Alloy IVa might satisfy this theory, if the amounts of aluminium, manganese, and copper were just sufficient to make the binary alloys Cu_3Al and Mn_3Al in the proper proportions to give its magnetic properties in Condition (1);

---

* *Loc. cit.* † *Loc. cit.* ‡ *Loc. cit.*
§ A. W. Hull, Phys. Rev. xiv. p. 540 (1919).
‖ *Loc. cit.*

but as well as could be estimated, there was no relative change in intensity of the patterns when the magnetic permeability was reduced to about one-sixth of its previous value. An ionization method would have to be adopted for precision measurements. Further, Alloy III *a* showed only one crystal pattern, though its magnetic properties were of ferromagnetic magnitude, and by Ross's theory two lattices should be present. It is difficult to obtain correspondence between this theory and the results of the present experiments.

Heusler's * explanation could be applied on the hypothesis that when the alloy was composed of certain proportions of the elements, as in Alloy III *a*, the complex compound $Al_x Cu_a Mn_{(3x-a)}$ crystallized completely in a face-centred cubic lattice with which were associated the weaker ferromagnetic properties, as in nickel and cobalt; while for other proportions the crystallization could occur in two ways—a face-centred cubic lattice of the same dimensions as before, and also a body-centred lattice which would be attributed to a new complex compound. Then the stronger ferromagnetic properties would be associated with this new centred lattice, just as in the case of iron.

There has been an attempt † to explain the Heusler alloys as a series of solid solutions for which there has been considerable direct evidence. The work of Andrews ‡ with zinc-copper alloys has shown that as much as 37 per cent. zinc may be dissolved in copper as a solid solution without altering the crystal habit of the copper. Above that percentage a centred cubic lattice appeared which was obtained in great purity with alloys of 50–60 per cent. zinc. It is possible that some such action takes place in the Heusler alloys. The manganese and aluminium may dissolve in the copper to form a solid solution, retaining the characteristic face-centred cubic lattice of copper but increasing its lattice constant from 3·60 Å.U. to 3·70 A.U. due to the intrusion of the large Mn-Al complex group, which, like the zinc in copper, would not be detected by X-ray analysis. But for certain proportions of the constituents or for certain conditions of casting there may be produced a new centred cubic lattice, due to the Mn-Al complex, in sufficient quantity to give a diffraction pattern. The body-centred cubic lattice is certainly not due to any of the constituent metals as tested initially. It is natural to suppose it to be an alloy crystal.

* *Loc. cit.*
† L. Guillet, *Soc. d'Encouragement, Rev. de met. Mem.* p. 87, 1906.
‡ *Loc. cit.*

The iron-nickel alloys investigated by Andrews [*] and Kirchner [†] have shown crystalline habit analogous to that of the Heusler alloys. A particular nickel steel containing about 25 per cent. nickel can exist in two magnetic states. In the non-magnetic condition the X-ray pattern was found to be that of a face-centred cubic lattice, while in the magnetic state, produced by chilling in liquid air, there was present as well a body-centred cubic lattice. Again, the more ferromagnetic properties were accompanied by crystals of the centred cubic system. Hopkinson [‡] found that these two states of nickel steel had different densities, viz. 8·15 and 7·98, for the non-magnetic and magnetic steels respectively. When these values were applied by Kirchner to determine the lattice constants for the crystals from the formulæ

$$d = \sqrt[3]{\frac{4 \cdot L}{N \cdot s}} \text{ for a face-centred cubic lattice}$$

and

$$d = \sqrt[3]{\frac{2 \cdot L}{N \cdot s}} \text{ for a body-centred cubic lattice,}$$

where L is the " mean " atomic weight of the alloy obtained from the composition of the alloy, N is Avogadro's number, and s is the density, he obtained very good agreement with his experimental values. The same was found to hold in the case of the Heusler alloys. For Alloy III a the density 7·26 gave a value $d = 3·60$ A.U. for the face-centred lattice, and from Alloy IVa of density 7·19 the value of the body-centred lattice constant $d = 2·86$ A.U., assuming that as an approximation the whole alloy was a body-centred cubic.

The attempt to produce a change in the diffraction pattern of the alloy by a magnetic field, due to the rotation or displacement of some magnetic particle, failed to give any positive result either in crystal lattice or in the intensity of the diffraction lines. This was to be expected from other experiments with X-rays. K. T. Compton and Trousdale [§] found that the Laue pattern through a crystal of pyrrhotite or magnetite was unaffected by the action of a strong magnetic field on the crystal. A more sensitive method by ionization employed by A. H. Compton and Rognley [‖] failed to detect any change in the intensity of reflexion from a crystal face of pyrrhotite when in a magnetic field. The

[*] *Loc. cit.*
[†] *Loc. cit.*
[‡] Proc. Roy. Soc. xlvii. p. 138 (1889).
[§] K. T. Compton and E. A. Trousdale, Phys. Rev. v. p. 315 (1915)
[‖] A. H. Compton and O. Rognley, Phys. Rev. xvi. p. 464 (1920)

absorption of gamma-rays by iron * was the same, no matter what the magnetic state of the iron. The only positive results with regard to the effect of a magnetic field on X-ray phenomena have been obtained by Forman † and Becker ‡. who have obtained distinct variations in the absorption co-efficients for X-rays of substances when placed in a magnetic field. The evidence to date points to the probable seat of magnetic phenomena in the behaviour and configuration of the outer or valence electrons. This, of course, is in agreement with the well-known changes in magnetic properties that take place as the result of chemical action, and those due to temperature variation which might be expected to have a direct influence on the loosely-bound valence electrons.

VII. SUMMARY.

1. The crystal structures of aluminium, copper, and manganese have been studied by X-ray methods. The first two metals crystallized in a face-centred cubic system of lattice constant 4·05 Å.U. and 3·60 Å.U. respectively. The crystal structure of manganese has not been solved.

2. A study of two Heusler alloys of definite compositions and magnetic properties has shown that they occurred in two crystal forms—one a face-centred cubic crystal of constant 3·70 Å.U., and the other a combination of this same face-centred cubic crystal and a body-centred cubic crystal of lattice constant 2·98 Å.U.

3. These crystal habits of the Heusler alloys have been discussed in relation to the theories of the alloys, and evidence has been adduced indicating that they may be considered as solid solutions of manganese-aluminium alloy in copper. This is tentative, pending further experiments.

4. In no case was there any indication of the free constituent metals in the alloys, showing that they are homogeneous within the limit of " sensitivity " of the method of analysis.

5. In agreement with the crystallographic data of the ferromagnetic elements—iron, nickel, cobalt, and the alloy iron-nickel, which can assume a non-magnetic or magnetic condition—the more ferromagnetic Heusler alloy contained a body-centred cubic lattice, while the more weakly ferromagnetic one showed only the face-centred cubic lattice.

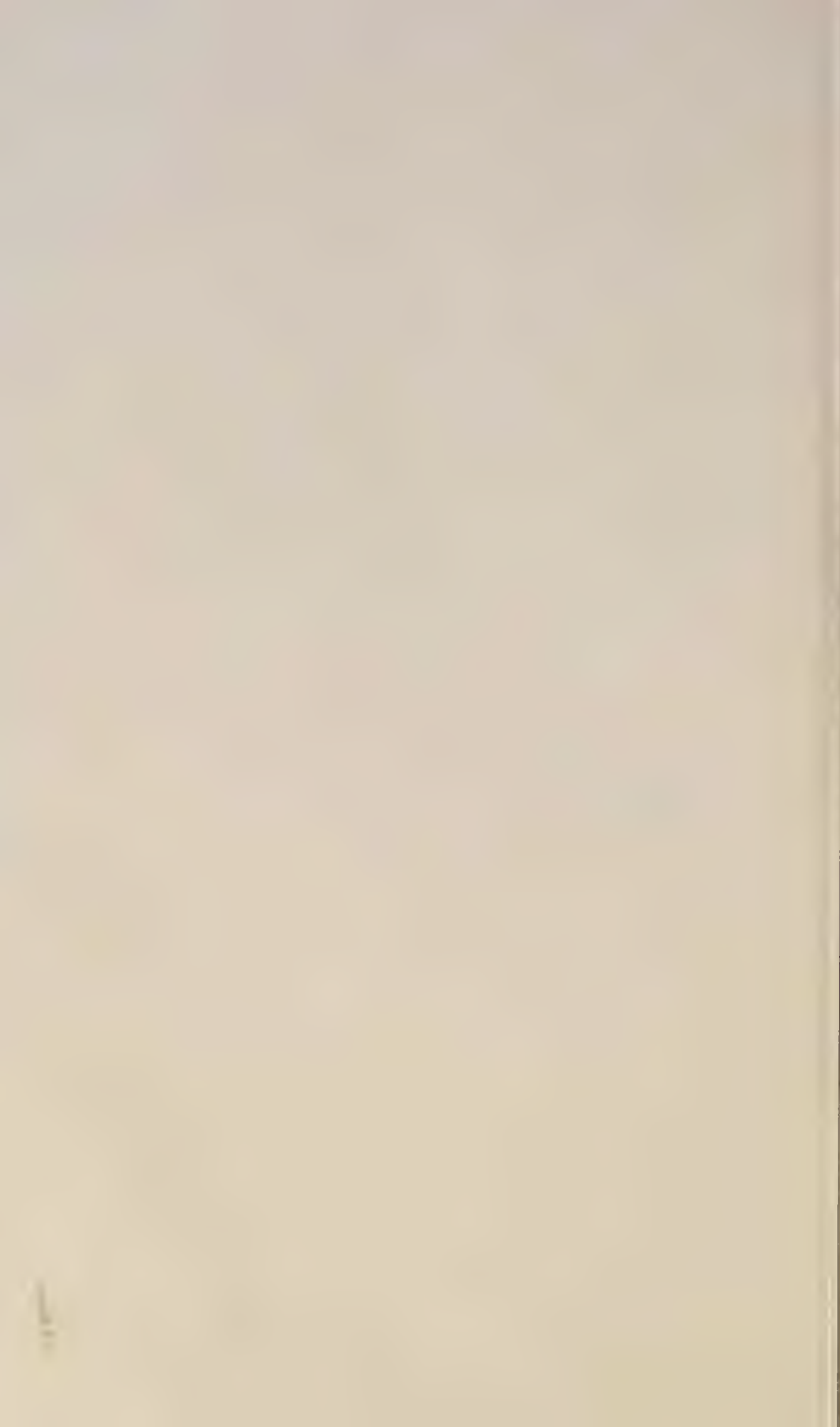6. The variation of the magnetic properties of an alloy of

* A. H. Compton, Phys. Rev. xvii. p. 38 (1921).
† A. H. Forman, Phys. Rev. iii. p. 306 (1914) ; vii. p. 119 (1916).
‡ J. A. Becker, Phys. Rev. xx. p. 134 (1922).

Young

Phil. Mag. Ser. 6. Vol. 46. Pl. IV.
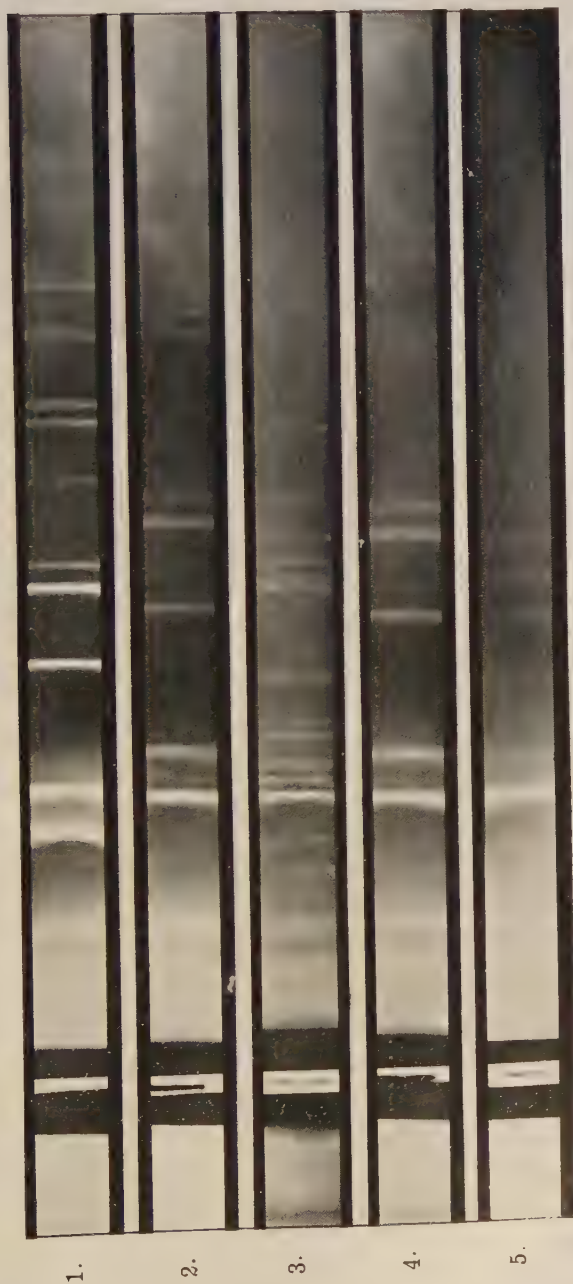
Powder Photographs of Al, Cu, Mn, Alloy III a and Alloy IV a in the order named.

1.

2.

3.

4.

5.

definite composition by suitable heat treatment produced no apparent change in the crystal form of the alloy.

7. The superposition of a magnetic field of 3500 gauss did not alter the crystal form of the alloys or make any noticeable change in the relative intensities of reflexion from the different crystal planes, indicating no change in orientation of the crystal unit.

8. Arguments have been presented tending to show that the ultimate magnetic unit is not the molecule or atom or any complex group of these, but that the magnetic effects are associated with the valence electrons.

XXIX. *Disintegration in Discharge Tubes.*
By H. P. WARAN, *M.A., Ph.D. (Cantab.), F.Inst.P.* [*]

[Plate V.]

1. *Historical.*

THE disintegration of discharge tubes may be divided broadly into two classes (*a*) the disintegration of the electrodes known as the sputtering, (*b*) the disintegration of the glass walls. Of these, the disintegration of the electrodes has been noted from very early times. Thus, as early as 1861, it had formed the subject matter of a paper by Gassiot [†] to the British Association. However, Sir William Crookes [‡] was the first to conduct a systematic investigation of the phenomenon using different metals for his electrodes. Recently Kohlschütter [§] and the research staff of the General Electric Co. [‖] have investigated the phenomenon in great detail. On the other hand, very little is known about the

---

[*] Communicated by Prof. A. W. Porter, D.Sc., F.R.S., F.Inst.P.
[†] Rep. Brit. Ass. ii. p. 38 (1861).
[‡] Proc. Roy. Soc. l. p. 88 (1891).
[§] *Jahrb. d. Rad. U. Elek.* ix. p. 355 (1912).
[‖] Phil. Mag. xlv. p. 98 (1923).

disintegration suffered by the glass walls, probably for the reason that its effects are not so very marked. But, as Dr. Coolidge * has pointed out, in X-ray tubes that have failed from the cracks resulting from the chipping off of the glass in the neighbourhood of the cathode, such disintegration is prominently noticed. In special cases where the effects get accentuated by a focussing of the ions, the intense local heating melts the glass, and the pressure of the external atmosphere blows in a hole of the type shown at X in fig. 1.

Fig. 1.
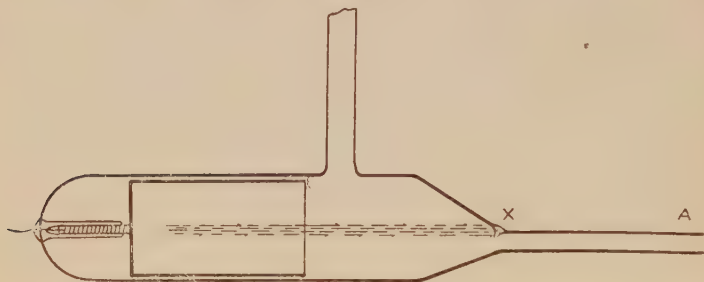
In the present case a cylinder of aluminium formed the electrode, sending out a concentrated axial pencil of ions that hit the glass at X, the tube A not having been blown quite axial with the cylindrical electrode. In an earlier paper † on the subject I drew attention to the curious type of channels cut on the glass walls when a discharge is deflected on to it by a transverse magnetic field.

2. *Effect of the positive ions.*

As in the case of cathodic sputtering the agency responsible for the observed effect is mainly the ionic bombardment of the walls. Such a bombardment may bring about the disintegration, either mechanically or thermally, or by a combination of both actions. The apparent characteristics of the convergent set of markings first obtained led me to the suggestion that the markings are of the nature of tracks left by the motion of the particles along the glass walls. In that case it is the kinetic energy of the ion that is responsible for it. The lightest positive ion of hydrogen has a velocity about a tenth of that of an electron, a mass nearly 2000

---

* Phys. Rev. xi. p. 409 (1913).
† Phil. Mag. xliii. p. 226 (1922).

times as great, and a kinetic energy about twenty times as great. Hence there was no doubt that the disintegration was produced mainly by the positive ions.

3. *A Mechanical Theory of Origin.*

The evidence in support of such a mechanical orgin might be summarized briefly as follows. Firstly, the short light scratches on the glass could be imagined as arising from the sand-blast action of the swiftly moving positive ions moving towards the cathode, an equality in the energy of the particles accounting for the nearly equal length of the markings. Secondly, the peculiar shape and convergency of the tracks as shown in fig. 2, may be due to the deflecting

Fig. 2.

Deflexion by field.
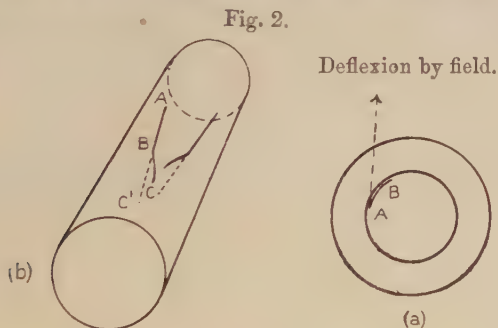
action of the transverse magnetic field. Let such a positive particle strike the cylindrical wall at A. So long as the particle has a sufficient forward velocity the magnetic field exerts a deflecting force at right angles to the axis of the tube. The cylindrical walls constraining such a motion, the particle can reach a higher level B only by travelling as shown in (*a*) along the cylindrical walls, and the track whose projection is A B is thus inclined to the axis of the tube. The bend BC towards the axis as shown at (*b*), may be due to the loss of velocity suffered by the particle after it has travelled the length AB, the particle of slower velocity being forced to a higher level C by motion along BC which is shorter than the straight path BC'.

Such an explanation, though fitting some of the facts observed, is obviously defective. For instance, in the absence of the magnetic field there is a uniform distribution of the positive particles across the cross-section of the discharge, and when they get deflected by the magnetic field

X 2

there is no reason why they are not striking the walls at azimuths other than those corresponding to the tracks observed. In fact, without any regularity, we ought to get a general corrosion of the glass. This point was tested with discharge tubes of the form shown in fig. 3.

Fig. 3.
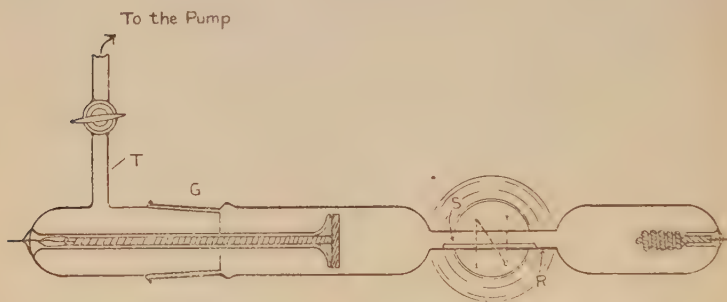
A large ground joint at G permitted the easy introduction and withdrawal of test surfaces S of glass, mica, etc., introduced into the narrow region R, placed between the poles of a large electromagnet. Even after repeated trials with different gases at different pressures no markings of any kind could be seen on the test surfaces.

4. *Energy Considerations.*

The observed tracks are in general about 2 millimetres in length, and about ½ millimetre in width, and their edges are quite ragged. Particles capable of effecting such a corrosion of the glass in virtue of their motion must have a very considerable energy associated with their motion. Goldsmith [*] has shown that positive rays of hydrogen can be made to have velocities of the order of 2×10^8 cm. a second, and that they pass readily through sheets of mica ·005 mm. thick. The particles from radioactive sources are known to be capable of penetrating glass and mica surfaces to a depth of over ·05 mm. and produce discoloration [†]. In a discharge tube the energy of the positive particle increases with the potential used for the discharge, and in a comparatively hard tube it would be interesting to examine the mechanical effect of positive rays on surfaces placed

* Physical Rev. ii. p. 16 (1913).
† Rutherford, Phil. Mag. xix. p. 192 (1910).

against their path and look for any tracks of their motion on the surface. For this purpose a tube of the form shown in fig. 4 was used. A is a wide tube over an inch in diameter, and C is a massive aluminium cathode of the shape shown, having a central aperture for letting out the positive rays. Behind the cathode the test surfaces were arranged, at an angle of about 20° to the path of the rays, on a suitable wire frame rigidly fixed to the glass walls. A simple form of Gaede Langmuir mercury vapour pump was used to exhaust the tube, and being connected up as shown, it kept the space behind the cathode exhausted to a very low pressure, so that the loss of energy of the positive rays by molecular collision was kept low. To keep up the discharge a steady feed of

Fig. 4.
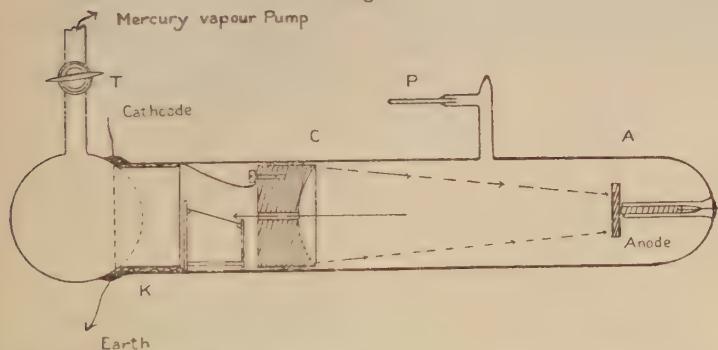
gas was introduced into the inter-electrode space through the platino-palladium tube P. Experimenting with glass and mica surfaces it was found that they got charged, and doubt was felt if the particles were not being deflected away by this charge. It was thought advisable to use conducting surfaces that could be earthed by a wire taken out through the wax joint at K. Though silvered surfaces are quite suitable for the purpose, it was thought better to use smoked surfaces of mica which are much more sensitive to any mechanical impact on them.

Experimenting with such an arrangement an intense beam of positive rays could be seen to strike the smoked surface causing an occasional scintillation, probably due to the disengaged smoke particles being raised to incandescence by the positive ray bombardment. Though the experiments were repeated at various gas pressures no traces of any tracks could be seen on the surface. However, within a few seconds of the bombardment there is a distinct change

in the reflecting power of the smoky surface over the area bombarded, indicating that the positive rays did produce a visible mechanical effect though of an order different from that expected. It was able to ruffle up the layer of carbon particles, which had a velvety structure of the type shown in fig. 5 (*a*), into a different orientation as indicated in fig. 5 (*b*) so that for the same angle of incidence the reflecting power of the two areas is different. By prolonging such positive ray bombardment for hours Stark and Wendt * have obtained actual evidence for the corrosion of surfaces of glass, mica, etc. They observe, however, that though quartz is no harder than glass, very little effect is observed on quartz surfaces. This throws a doubt on the mechanical theory for the disintegration of glass surfaces. Further, positive ions having energies of this order are never met with under the conditions of our experiment where comparatively high gas

Fig. 5.

(a)   (b)
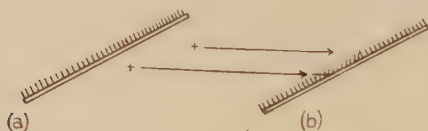
pressures and low potential discharges are used. Thus, though it is possible that the positive ion bombardment may be indirectly assisting the formation of such markings, the marks themselves can never be regarded as the tracks left by the motion of the positive particles along the walls.

5. *Connexion with the striations.*

An interesting property of these marks on the glass surface is their regularity and symmetry of distribution along the axis of the tube, a property displayed also by the striations, and it seemed possible that there might be some connexion between the two. In both cases of these phenomena the spacing has been found to vary with the gas pressure, and they are found to develop most readily in the case of discharge through carbon gases, which are noted for giving well marked cup-shaped striations. They are also found to lose their regularity when the positive column and the striations have ceased to exist. Thus, there is no doubt that the striations are intimately connected with such regularity as is observed in these marks.
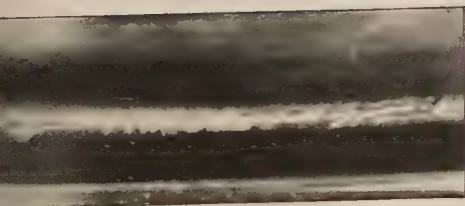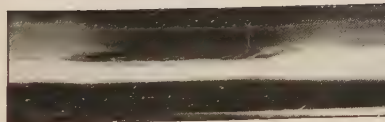
* *Ann. der Physik*, xxxviii. p. 921 (1912).

(a)
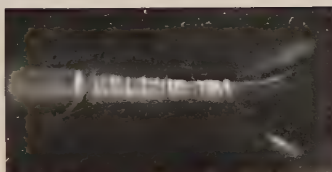
(b)

(c)

(d)

6. *A Thermal explanation for the marks.*

We have seen that the localized heating effect of ionic bombardment is very considerable. Stark and Wendt have observed that the surface gets quite red hot over the area bombarded. Quincke * by his extensive researches on the thermal properties of glass has shown that in the neighbourhood of an electric discharge the localized heat might be sufficient to melt a superficial layer of glass, and on its subsequent solidification and cooling superficial fractures are developed. On such a thermal view of the phenomenon the observed difference between the behaviour of quartz and glass is only to be expected. The melting point of quartz is much higher than that of glass and, notwithstanding its higher thermal conductivity, even if a superficial layer of quartz does get fused it is not likely to develop cracks on cooling, since the coefficient of expansion of fused silica is very much lower than that of glass or quartz.

Such a thermal view of the phenomenon seems to be quite applicable to the type of disintegration under discussion even when the potential used to excite the tube is comparatively low. Though the positive particles have a higher energy at lower gas pressures the thermal effect might be greater at higher gas pressures when the current through the tube is a maximum, and the ionization by collision results in the production of a very large number of ions. It is also at this stage that the striations are most pronounced and the markings on the glass walls developed most readily. Further, R. W. Wood † has shown that corresponding to the striations there are zones of maximum heating in a discharge tube. Such zones of heating would be particularly pronounced when the striations are squeezed together into a small area by the deflecting field. An examination of the deflected discharge reveals the presence of the striations in it, and the observed markings on the sides of the tube are found to correspond to these striations. But straight line cracks at right angles to the axis of the tube as shown in Pl. V. (*a*) and (*b*), and irregular wavy cracks of the type shown in Pl. V. (*c*) and (*d*), are also frequently met with.

Even in the absence of a deflecting magnetic field cracks and markings of this nature are often found in discharge tubes, especially in the neighbourhood of the electrodes. Such defects develop rapidly, especially in the presence of

* *Ann. der Physik*, xlviii. p. 113 (1915).
† Wied. *Ann.* xxxix. p. 238 (1896).

an initial deformation in the form of a scratch or opened air line in glass. Intense local heating is noticeable in such regions, and a number of minute cracks may also be seen on a microscopic examination of the surface. The existence of such incipient cracks in discharge tubes is proved by at least one well known observation. They have a marked tendency to crack off on the application of a blow-pipe flame, a tendency shared also by glasses that have long been in contact with radioactive material.

In conclusion I beg to express my indebtedness to the kind and sympathetic advice and guidance of Prof. A. W. Porter, D.Sc., F.R.S., in this work done at his laboratory.

XXX. *The Velocity Constant of a Unimolecular Reaction.* *By* James Rice, *M.A.*[*]

SEVERAL investigators have, during the past few years, devoted their attention to the elucidation of the problem of chemical reaction from its statistical side, basing their arguments either on purely statistical considerations or on a theory as to the nature of chemical reaction itself and the causes provoking it. At the same time free use has been made of some form of the Quantum hypothesis. A brief account of these researches will be found at the beginning of the paper by Mr. McKeown which follows this communication.

It would appear that the following formula for κ, the velocity constant of a unimolecular reaction, finds some experimental support, at least in the case of gaseous reactions; it is

$$\kappa = s \exp(-\epsilon/kT), \quad . \quad . \quad . \quad . \quad (1)$$

where s and ϵ are constants for a given compound dissociating into two components, and k and T have their usual significance. The quantity ϵ is an amount of energy, usually called the "critical increment," and s, on simple dimensional grounds, must be a frequency. If one adopts the standpoint of the Quantum theory it is plausible to write

$$\epsilon = h\nu$$

and regard ν as the frequency of some oscillatory process going on within the molecule, which leads to a rupture of the molecule when the amplitude of vibration has

* Communicated by Prof. W. C. M. Lewis.

increased to such a point that the energy equals one quantum of energy for this frequency. On grounds which are largely empirical Dushman * has suggested that s should also be equated to ν, so that (1) should read

$$\kappa = \nu \exp\left(-h\nu/k\mathrm{T}\right). \quad . \quad . \quad . \quad . \quad (2)$$

The object of this paper is to indicate that Dushman's equation (2), or one closely approximating to it, can be deduced very readily by a plausible " quantization " of an expression obtained some years ago by the writer and given by him in a discussion on Catalysis at the British Association meeting of 1915.

In order not to render the analysis unduly cumbersome we assume that for the purpose in view a molecule may be adequately represented by a simple mechanical model, in which two bodies are imagined as bound by a quasi-elastic force. We are only concerned with one coordinate which represents the distance apart of the two components and which is denoted by q. The introduction of other co-ordinates specifying all the remaining degrees of freedom of the molecule is unnecessary and would only serve to complicate the analysis with multiple integrals, which would disappear by cancellation in the final result. We assume that q may have any value from zero to infinity, and that the mutual potential energy, $\phi(q)$, of the two components increases with q until the separation $q=c$ is reached ; beyond the critical distance, c, the potential energy either decreases or remains constant. In the first case a supply of energy is required to enable the dissociated parts once more to enter into union : in the second case no energy is needed to ensure combination if the two constituents should encounter one another.

The energy of such a mechanism is given by

$$\epsilon = a\dot{q}^2 + \phi(q),$$

where a is in general a function of q.

The momentum is given by

$$p = 2a\dot{q}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and so

$$\epsilon = p^2/4a + \phi(q).$$

Consider a system made up of such molecules, and let such an interaction take place between the molecules, or between these molecules and some other agent, such as gas molecules

* J. Amer. Chem. Soc. xliii. p. 397 (1921).

or radiation, as is sufficient to bring about an exchange of energy between the various elements of the system. The exact nature of the means by which such exchange is produced is a matter surrounded with well-known difficulties, but the argument which follows is not immediately concerned with it and, being based on the existence of a state of equilibrium, is purely statistical. In such a state there will be present a definite number of undissociated molecules and also a definite number of the dissociated parts. The individuals in these two groups will change, but not their relative numbers. It is our business to calculate how many of the molecules will dissociate per second; this will, of course, be the number of pairs which recombine per second.

The number of undissociated molecules which are in the phase-extension q, p to $q + dq, p + dp$ is

$$A e^{-\mu \epsilon} dq\, dp,$$

where $\mu = 1/k\mathrm{T}$ and A is a constant *.

We can represent the number of undissociated molecules by the double integral,

$$A \int_0^c \int_{-\infty}^{\infty} e^{-\mu \epsilon} dq\, dp. \quad . \quad . \quad . \quad . \quad (4)$$

The average value of any property, f, of these molecules is

$$\frac{\int_0^c \int_{-\infty}^{\infty} f e^{-\mu \epsilon} dq\, dp}{\int_0^c \int_{-\infty}^{\infty} e^{-\mu \epsilon} dq\, dp}. \quad . \quad . \quad . \quad (5)$$

The rate at which the molecules dissociate is the rate at which they attain the condition in which q has increased numerically from a smaller value to the value c. The method of calculation is familiar. The number of molecules in the phase-extension $c - \dot{q}\, \delta t, p$ to $c, p + dp$ is obtained.

---

* It is of course possible to question the validity of this expression under actual experimental conditions where a chemical reaction is going on and a state of statistical equilibrium between "reactants" and "resultants" has not been attained. However, in the case of those reactions which proceed at a rate sufficiently slow to enable measures of κ to be made, the critical condition for a molecule is so far removed from the average state that relatively few molecules are in this condition at one instant and their dissociation has but little influence on the statistical state of the undissociated molecules. In fact the use of the Maxwell distribution law here seems to be as justifiable as its use in the familiar treatment of viscosity and diffusion in the case of gases.

These will have passed the critical condition after an interval δt has elapsed *. Since $\dot{q} = p/2a$, the number is

$$A \exp \left\{ -\mu \left[\phi(c) + p^2/4a \right] \right\} p \, \delta t \, dp / 2a. \quad . \quad . \quad (6)$$

Integrating from $p = 0$ to $p = \infty$ and omitting δt, we obtain the rate of dissociation. It is

$$A e^{-\mu \phi(c)} \int_0^\infty e^{-a p^2} p \, dp / 2a,$$

where $\alpha = \mu/4a$.

This is equal to

$$A e^{-\mu \phi(c)} / 4 \alpha a$$

$$= k T A e^{-\mu \phi(c)}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The velocity constant, κ, is the quotient of (7) by (4),

$$\kappa = \frac{k T e^{-\mu \phi(c)}}{\int_0^c \int_{-\infty}^\infty e^{-\mu \epsilon} \, dq \, dp} \quad . \quad . \quad . \quad . \quad (8)$$

Since

$$\log \kappa = \log (kT) - \phi(c) / kT - \log \int_0^c \int_{-\infty}^\infty \exp (-\epsilon/kT) \, dq \, dp,$$

it follows that

$$\frac{d \log \kappa}{dT} = \frac{1}{T} + \frac{\phi(c)}{kT^2} - \frac{\int_0^c \int_{-\infty}^\infty \epsilon \exp (-\epsilon/kT) \, dq \, dp}{kT^2 \int_0^c \int_{-\infty}^\infty \exp (-\epsilon/kT) \, dq \, dp}$$

by (5)

$$= \frac{\phi(c) - \bar{\epsilon} + kT}{kT^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or practically

$$\frac{d \log \kappa}{dT} = \frac{\phi(c)}{kT^2}, \quad . \quad . \quad . \quad . \quad (9')$$

if the critical potential is large compared with the average energy of an undissociated molecule. This is now a well-known result and can easily be extended to a more general type of molecule, as Marcelin † first pointed out.

As stated previously the writer's object is to point out that if the expression (8) is modified in any one of several ways suggested by Quantum considerations, formulæ approximating to that of Dushman are obtained.

---

* In order to avoid a digression we are overlooking an important point to which a reference will be made presently.

† *Ann. de Physique*, iii. p. 120 (1915).

The most obvious suggestion is to assign to the molecular model the properties of an harmonic oscillator ; *i. e.*, to regard a as a constant and put $\phi(q)$ equal to bq^2, where b is another constant, so that the frequency of oscillation is given by

$$2\pi\nu = (b/a)^{\frac{1}{2}}.$$

The denominator in (8) then becomes

$$\int_0^c \int_{-\infty}^{\infty} \exp\left(-\alpha p^2 + \beta q^2\right) dq\, dp,$$

where $\beta = \mu b$.

This expression $= (\pi/\alpha)^{\frac{1}{2}} \int_0^c e^{-\beta q^2} dq$

$$= (\pi/\alpha\beta)^{\frac{1}{2}} \int_0^{c\sqrt{\beta}} e^{-x^2} dx.$$

Since $\beta c^2 = bc^2/k\mathrm{T}$, the integral approximates to $\pi^{\frac{1}{2}}/2$ if the critical potential energy be large enough compared with $k\mathrm{T}$; *e. g.*, if $bc^2 = 4k\mathrm{T}$, so that $c\sqrt{\beta} = 2$, the integral $= \cdot 995\, \pi^{\frac{1}{2}}/2$. Even if bc^2 is only equal to $k\mathrm{T}$ the integral is $\cdot 843$ times $\pi^{\frac{1}{2}}/2$.

Hence the denominator in (8) is approximately equal to

$$\cdot 5\, \pi \left/ (\alpha\beta)^{\frac{1}{2}} \right.$$

$$= \frac{\pi}{\mu\, (b/a)^{\frac{1}{2}}}$$

$$= \frac{k\mathrm{T}}{2\nu}.$$

Hence

$$k = 2\nu\, e^{-\mu\, \Phi(c)}.$$

If we assume that the critical potential energy is equal to $h\nu$, we have

$$\kappa = 2\nu \exp\left(-h\nu/k\mathrm{T}\right), \quad . \quad . \quad . \quad (10)$$

which is Dushman's expression multiplied by 2.

But Planck's treatment of the interaction of matter and radiation by means of an harmonic oscillator suggests that we might proceed with the quantization of (8) in a different manner. Thus considering a q, p diagram for the model we imagine it divided into annular elements by the curves of constant energy,

$$bq^2 + p^2/4a = \epsilon.$$

It is well known that the area of the elementary elliptical ring between the curves corresponding to ϵ and $\epsilon + d\epsilon$ is $d\epsilon/\nu$.

Let us postulate that all those molecules whose representative points lie within the ellipse of constant energy whose area is nh, are undissociated. This is equivalent to the assumption that dissociation takes place when the *whole* energy (attached to the coordinate q) reaches the critical value of n quanta, $nh\nu$, and not the potential energy alone. The number of molecules dissociating in time δt will then be represented by points in the q, p diagram lying sufficiently near to two of the quadrantal arcs of the nh ellipse.

It is necessary to point out before proceeding that we are involved in two assumptions here. The first is that the arrival of a representative point at the first and third quadrantal arcs of the critical ellipse is equivalent to a rupture of the molecule. To justify this we might say that at all events the molecule has become "active"; within a fraction of its period of oscillation the representative point, even without any further energy being acquired by the molecule, will have arrived at the position $q = c$, and the molecular configuration will be critical. The second assumption is concerned with a point which, as stated in the footnote on p. 315, was deferred for later consideration. In arriving at expression (6), we were clearly assuming that the molecule had sufficient energy to carry it up to the critical condition from the configuration $q = c - \dot{q}\,\delta t$. The calculation is purely kinematic and is of a type familiar in the kinetic theory of gases when treating viscosity, diffusion, etc. But in the gas applications the molecule is assumed to be on a *free* path with no retarding force acting on it, and it is legitimate to assume that it will maintain its velocity $\dot{q}$ unchanged for the element of time δt and so will actually travel the distance $\dot{q}\,\delta t$ as postulated in the calculation. But in the model assumed here, the separation of the molecular components is retarded by an attractive force and thus if the molecule is going to dissociate we must assume that the representative points of the molecules involved in expression (6) lie outside the constant energy curve

$$p^2/4a + \phi(q) = \phi(c).$$

Since the p coordinate of a point on this curve approaches the value zero as its q coordinate approaches c, we can satisfy this proviso if δt be taken sufficiently small. But in facing a similar difficulty with the idea that the "inactive" molecules are those represented by points within the critical energy curve we cannot dispose of it in so ready a manner. A point within this ellipse will not reach it, no matter how

near it is initially, *unless energy is supplied to the corresponding molecule.* Kinematically, the number of points reaching the ellipse in the time δt will be obtained by integrating

$$2\mathrm{A}\,e^{-n\mu\,h\nu}\,\dot{q}\,\delta t\,dp$$

from $p=0$ to $p=p_m$, where p_m is the maximum value possible for a point on the ellipse, so that $p_m^2/4a=n\,h\nu$. But, dynamically, we must postulate a supply of energy to the molecule during the interval δt, sufficient to maintain $\dot{q}$ constant in order to justify this expression. A further treatment of this point seems desirable, but as this paper is concerned with the discovery of a statistical basis for Dushman's formula, the assumption will be made without further discussion at present. The writer hopes to return to this matter in a subsequent communication, as it appears to have some bearing on the well-known difficulty in the radiation theory of chemical reaction, pointed out some time ago in this journal by W. C. M. Lewis *.

Proceeding with the argument as before, we obtain for the rate of dissociation of the molecules,

$$2\mathrm{A}\,e^{-n\mu\,h\nu}\int_0^{p_m} p\,dp \,/\, 2a$$
$$= \mathrm{A}e^{-n\mu\,h\nu}\,p_m^2 \,/\, 2a$$
$$= 2\mathrm{A}\,e^{-n\mu\,h\nu}\,n\,h\nu.$$

Under the circumstances (4) would apparently become

$$\mathrm{A}\int_0^{nh} e^{-\mu\epsilon}\,d(\epsilon/\nu),$$

which is equal to

$$\mathrm{A}\int_0^{n\,h\nu} e^{-\mu\epsilon}\,d\epsilon/\nu$$
$$= \mathrm{A}(1-e^{-n\mu\,h\nu})/\mu\nu,$$

so that κ should be given by

$$\kappa = \frac{2n\,h\nu\,e^{-n\mu\,h\nu}}{(\mu\nu)^{-1}(1-e^{-n\mu\,h\nu})}$$
$$= 2n\,\frac{h\nu^2}{k\mathrm{T}}\,\frac{1}{\exp\,(n\,h\nu/k\mathrm{T})-1}. \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

However, (11) is based on a partial application of the Quantum hypothesis, and requires reconsideration.

In that form of the theory which permits every point on

* Phil. Mag. xxxix. p. 26 (1920).

the q, p diagram to represent an admissible physical state, it is nevertheless assumed that the Maxwellian law of distribution is modified by the postulate of finite regions of equal probability. For an harmonic oscillator these regions are the ellipse and the successive elliptic annuli, all of area h, which are bounded by the ellipses of constant energy which enclose area $h, 2h, 3h$, etc. Thus if there be N oscillators whose representative points lie in the first region, there are $N e^{-\mu h \nu}$ with the points in the second, $N e^{-2\mu h \nu}$ in the third, and so on. This will modify the preceding calculation as follows. The number of molecules dissociating in time δt will be obtained by integrating

$$2 \frac{N e^{-(n-1)\mu h \nu}}{h} \dot{q} \, \delta t \, dp,$$

since the density in phase of molecules whose points are in the nth finite region is

$$\frac{N e^{-(n-1)\mu h \nu}}{h}.$$

Hence the rate of dissociation is obtained as before to be

$$\frac{N e^{-(n-1)\mu h \nu}}{2ah} p_m^2$$

$$= \frac{2N e^{-(n-1)\mu h \nu}}{h} n h \nu$$

$$= 2n\nu N e^{-(n-1)\mu h \nu}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

The number of undissociated molecules is

$$N(1 + e^{-\mu h \nu} + e^{-2\mu h \nu} + \ldots + e^{-(n-1)\mu h \nu})$$

$$= N \frac{1 - e^{-nh\mu\nu}}{1 - e^{-\mu h \nu}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

Dividing (13) by (12) we obtain

$$\kappa = 2n\nu \frac{e^{\mu h \nu} - 1}{e^{n\mu h \nu} - 1}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (14)$$

If $h\nu/kT$ be sufficiently large

$$\kappa = 2n\nu \, e^{-(n-1)\mu h \nu}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (15)$$

and it is easy to deduce that

$$\frac{d \log \kappa}{dT} = \frac{(n-1) h \nu}{kT^2}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (16)$$

So if we write $\nu' = (n-1)\nu$, we have

$$\kappa = \frac{2n}{n-1} \nu' \exp(-h\nu'/kT). \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (17)$$

For purposes of numerical calculation (17) approximates to Dushman's formula, except for the factor 2, provided ν' is calculated in the usual way from the equation for $d \log \kappa/dT$ which becomes

$$\frac{d \log \kappa}{dT} = \frac{h\nu'}{kT^2}.$$

It should be observed that this result does not imply that an absorption band will be found at ν', but possibly only at a submultiple of it.

If ν were too small (15) and (16) would not be so exact, and (14) would have to be used. Provided n were sufficiently great

$$\kappa = 2n\nu \, e^{-(n-1)\mu h\nu} (1 - e^{-\mu h\nu}). \quad . \quad . \quad (18)$$

This would produce a small change in (16), which would became

$$\frac{d \log \kappa}{dT} = \frac{h\nu}{kT^2}\Big(n - 1 - \frac{1}{\exp{(h\nu/kT)} - 1}\Big). \quad . \quad (19)$$

If n be unity, we obtain the peculiar result,

$$\kappa = 2\nu.$$

So that the assumption that the molecule ruptures for a critical energy of one quantum appears to lead to an enormous velocity-constant and one which is independent of temperature.

But, of course, Dushman's result is known not to be generally true. Its success seems to lie in gaseous reactions. This attempt to base it on statistical reasoning shows that it probably holds when the mechanism of the reaction is analogous to some such simple concept as the harmonic oscillator ; but is altogether inadequate if the nature of the reaction is more complex.

These quantizations clearly rest on the implication that all physical states represented by a point on the q, p diagram are admissible. If we adopt the form of the Quantum theory, known as the " Stationary States hypothesis," which is employed in present-day atomic theories and in which only the points on the region boundaries represent admissible states, our method fails. One must start *ab initio* from postulates based on *à priori* probabilities of these states. Mr. McKeown shows in the following paper how the reasoning runs in that case.

George Holt Physics Laboratory,
    University of Liverpool.

XXXI. *The Velocity of a Unimolecular Reaction.*
By A. McKeown, *M.Sc.*[*]

THE physical basis of unimolecular chemical processes
has received considerable attention during the last
few years. A semi-empirical method of investigation
employed by Herzfeld (*Ann. der Physik*, lix. p. 613, 1919)
depends on a combination of Stern's expression for the
equilibrium constant of a unimolecular decomposition into
atoms with the velocity of union of the atoms as given
by the well-known collision expression. The resulting
equation for the specific velocity of decomposition (velocity
constant) is

$$k_1 = \frac{k\mathrm{T}}{h} e^{-Q/k\mathrm{T}}(1 - e^{-h\nu_1/k\mathrm{T}}),$$

where k, h, T have their usual significance, Q is the heat of
reaction per molecule, and ν_1 is the frequency of vibration
of the atoms in the molecule. Dushman (Journ. Amer.
Chem. Soc. xliii. p. 397, 1921) has recently compared the
consequences of this formula with observation, and finds
that the values of ν_1 calculated are many times greater than
those deduced from specific heat data.

Such a method of approach as the above gives us no clue
as to the mechanism of the unimolecular process itself ; and,
indeed, the expression for k_1 may vary in form, depending
on the particular degrees of freedom chosen as active in the
molecule. Thus Trautz (*Zeitsch. für Physik*, ii. p. 113, 1920),
working along similar lines, assumes no vibration of the atoms
in the molecule, and his resulting expression is therefore

$$k_1 = \frac{k\mathrm{T}}{h} \cdot e^{-Q/k\mathrm{T}}.$$

For the radiation theory of chemical change, advanced by
various writers during the last few years, the case of uni-
molecular processes has a special interest as distinct from
reactions of higher order. In the case of a bimolecular
reaction, the primary process of activation of the molecules
by radiation is assumed to be very fast, so that the observed
rate of reaction itself is governed only by the rate of collision
of activated molecules. For the unimolecular case, however,
collisions can play no part, and the velocity of dissociation
should be governed by that of the process of activation—
that is, the actual rate of interaction of matter and radiation
should give an upper limiting value to the observed rate of
chemical change.

* Communicated by Prof. W. C. M. Lewis.

Working on this basis, W. C. M. Lewis (Phil. Mag. xxxix. p. 26, 1920) has attempted to obtain a value for k_1 by equating the velocity of decomposition to the rate at which molecules obtain their critical increment $h\nu$ by absorption from the surrounding radiation field. On the view of continuous absorption in accordance with Planck's second formulation of the quantum theory, the resulting expression for k_1 is found to give values very much smaller than such velocity constants as have been experimentally observed. More recently, Lewis and McKeown (Journ. Amer. Chem. Soc. xliii. p. 1297, 1921) have attempted to account for this very great discrepancy, whilst retaining the concept of continuous absorption of radiation, by ascribing to the molecular field of action a concentrating effect, or what is the equivalent of a very high and practically constant refractive index of the order 200. Certain justifications of such an assumption have been offered, but whilst the expression obtained agrees well with observation it is felt that the picture realized is at best a very crude representation of the actual mode of interaction between radiation and matter.

Attempts have also been made by Lewis (*loc. cit.*) and Rideal (Phil. Mag. xl. p. 461, 1920) to apply the Einstein concept of discrete quanta of radiant energy to the case of a unimolecular chemical reaction. Activation of a molecule is considered to take place by collision with a quantum of the frequency corresponding to the activation process. Lewis ascribes to the quantum the diameter 10^{-13} cm., whilst Rideal gives a value equal to the wave-length of the quantum itself. The velocity of the quantum is put equal to the velocity of light. Both writers, however, make use of an erroneous expression for collision frequency, so that their final results are invalid.

Dushman (*loc. cit.*) has suggested an empirical formula for the unimolecular velocity constant, viz. :

$$k_1 = \nu \cdot e^{-h\nu/kT},$$

and has shown this to be in agreement with existing experimental data (*cf.* Tolman, Journ. Amer. Chem. Soc. xliii. p. 269, 1921). The factor $e^{-h\nu/kT}$ represents the fraction of activated molecules present at any instant, and the frequency factor ν, identical with that in the exponential term, is taken to denote the frequency of some intra-molecular occurrence necessary for the decomposition of an activated molecule. Christiansen (*Zeitsch. für physik. Chem.* ciii. p. 91, 1922), in a discussion of the problem, has attempted to obtain a theoretical justification of Dushman's equation using

Einstein's particular conception of the mechanism of energy exchanges between molecules and radiation (*Physik. Zeitsch.* xviii. p. 121, 1917). Christiansen assumes that the process of activation corresponds to passage of a molecule by absorption of radiant energy from the normal state n to the activated state m, the difference of energy contents of these states being $\epsilon_m - \epsilon_n = h\nu$. If this difference be great, the number of molecules in the activated state under equilibrium conditions may be written :

$$N_m = N \cdot \frac{p_m}{p_n} \cdot e^{-h\nu/kT},$$

where N is the total number of molecules, and p_n, p_m denote the respective *a priori* probabilities of the states in question [*]. When chemical change is possible, an activated molecule may either revert by emission to its normal state n or may pass by emission to another state n', the latter passage being identified with the chemical decomposition. The states m and n' are also connected by the Bohr relation :

$$\epsilon_m - \epsilon_{n'} = h\nu'.$$

According to Einstein the probability of the change $m \rightarrow n'$ may be written equal to $\left(A_m^{n'} + B_m^{n'} u_{\nu'} \right)$, where the first term is the probability of spontaneous emission, and the second is the probability of the change occurring under the action of the thermal radiation field. Hence the rate of chemical change, which is controlled by this process, is

$$k_1 = \frac{p_m}{p_n} \cdot e^{-h\nu/kT} \left(A_m^{n'} + B_m^{n'} u_{\nu'} \right),$$

or using Einstein's expression for $u_{\nu'}$,

$$k_1 = \frac{p_m}{p_n} \cdot e^{-h\nu/kT} \cdot \frac{A_m^{n'}}{1 - e^{-h\nu'/kT}}.$$

Christiansen now assumes that the term $A_m^{n'}$ which denotes the probability of the spontaneous change $m \rightarrow n'$ may be written equal to ν', the frequency characteristic of the change. With this substitution his equation reduces to

$$k_1 = \frac{p_m}{p_n} \cdot e^{-h\nu/kT} \cdot \frac{\nu'}{1 - e^{-h\nu'/kT}}.$$

[*] These *a priori* probabilities take account of the fact that each quantum state of definite energy content of a molecule may be realized in different ways, the p's representing the number of possible modes of realization of each state.

For the case of small values of $\frac{h\nu'}{kT}$ this formula approximates to

$$k_1 = \frac{p_m}{p_n} \cdot \frac{kT}{h} \cdot e^{-h\nu'/kT},$$

comparable with the Herzfeld expression. For large values of $\frac{h\nu'}{kT}$ Christiansen shows that the formula reduces to

$$k_1 \doteqdot \frac{p_m}{p_n} \cdot \nu' \cdot e^{-h\nu'/kT},$$

which bears a close formal resemblance to that of Dushman, the frequency ν' being, however, essentially different from that occurring in the exponential.

It will be observed that the mathematical treatment of Christiansen is very analogous to the interpretation which Dushman gives to his equation. Both writers assume the possibility of the actual existence of activated molecules as apart from the dissociation products. Dushman then ascribes the decomposition of an activated molecule to coincidence of the state of activation with a particular static configuration of the molecule, this configuration occurring ν times per second. Christiansen, however, associates the decomposition of an activated molecule with the occurrence of a more catastrophic phenomenon—the change $m \rightarrow n'$ which takes place (for large values of ν') approximately ν' times per second. Christiansen's method of attack is the more revolutionary, and really involves a new and somewhat startling quantum electrodynamics, since he ascribes definite values to the A's and B's of Einstein's quantum dynamics, hitherto left undetermined by Einstein himself. This will be more clearly seen in the following treatment, which differs somewhat from that of Christiansen in that the separate existence of active molecules is not assumed, and therefore the rate of the dissociation is governed solely by the process of activation itself.

Consider a gas composed of similar molecules in equilibrium with temperature radiation (no chemical change assumed), each molecule capable of existing in a discrete series of states with energy contents $\epsilon_1,\ \epsilon_2,\ \epsilon_3,\ \dots$. In statistical equilibrium the numbers of molecules in the nth and mth states are given by

$$N_n = N \cdot A \cdot p_n \cdot e^{-\epsilon_n/kT}$$

and

$$N_m = N \cdot A \cdot p_m \cdot e^{-\epsilon_m/kT}$$

where p_m and p_n are the *a priori* probabilities of the states in question, and A is a factor independent of the state. Following Einstein, the probabilities of the transitions $n \to m$ and $m \to n$ in the time interval dt are :

$$d\pi_{n \to m} = B_n^m u_\nu dt \quad \text{and} \quad d\pi_{m \to n} = (A_m^n + B_m^n u_\nu)\, dt,$$

where u_ν is the radiation density factor for the frequency ν corresponding to the changes $n \rightleftharpoons m$. It follows that for statistical equilibrium

$$A_m^n p_m = u_\nu \left(B_n^m . p_n . e^{\overline{\epsilon_m - \epsilon_n}/k\mathrm{T}} - B_m^n p_m \right).$$

If u_ν increases without limit as T increases, then

$$B_n^m p_n = B_m^n p_m.$$

Writing $A_m^n/B_m^n = \mathrm{K}$, Einstein obtains :

$$u_\nu = \mathrm{K}/(e^{\overline{\epsilon_m - \epsilon_n}/k\mathrm{T}} - 1).$$

Comparison with Planck's radiation formula shows that

$$\epsilon_m - \epsilon_n = h\nu$$

and

$$\mathrm{K} = 8\pi h\nu^3/c^3.$$

Let us now assume, by analogy with Christiansen, that the probability per unit time of the spontaneous emission process $m \to n$ is in general equal to ν. It follows that B_m^n is equal to $c^3/8\pi h\nu^2$, and therefore also in general :

$$B_n^m = \frac{p_m}{p_n} . B_m^n = \frac{p_m}{p_n} . \frac{c^3}{8\pi h\nu^2}.$$

Hence the number of transformations $n \to m$ per second in our system is given by

$$\mathrm{N}_n . \frac{p_m}{p_n} . \frac{\nu}{e^{h\nu/k\mathrm{T}} - 1}.$$

In a chemical system undergoing unimolecular decomposition, we may now consider that activation corresponds to the transition from the normal state n to the activated state m, and that the decomposition of an activated molecule is enormously more probable than the reversal $m \to n$, or, what seems more likely, that the activated molecule is identical with the decomposition products. The velocity of dissociation is then given directly by the rate of activation, and therefore by the above expression. For practically all

cases considered the ν term is 10^{14} to 10^{15}, and therefore $\frac{h\nu}{k\mathrm{T}}$ is large compared with unity. Consequently N_n reduces to N and $(e^{h\nu/k\mathrm{T}}-1)$ to $e^{h\nu/k\mathrm{T}}$. Hence we obtain finally for the velocity constant of unimolecular decomposition :

$$k_1 = \frac{p_m}{p_n} \cdot \nu \cdot e^{-h\nu/k\mathrm{T}}.$$

This equation differs from that of Dushman only in the factor $\frac{p_m}{p_n}$ which may be greater or less than unity. For Bohr orbits in the generalized Sommerfeld sense, p_m would be greater than p_n, but in no case would $\frac{p_m}{p_n}$ be a large numerical factor.

It will be obvious that the result obtained depends primarily on the assumption that $\mathrm{A}_m''=\nu$—that is, that the life of a stationary state m is equal, in the absence of radiation, to the period which characterizes the transitions $n \rightleftharpoons m$. The corresponding rate of absorption from a radiation field is very much greater than that given by classical electrodynamics. It may be noted that the expression for this rate does not contain in itself any of the properties of the absorbing system except the frequency ν, and even this is only associated with the system for a particular transition.

The law of spontaneous emission should be that which governs radioactive transformations, unless these are dependent in some way on a very penetrating external radiation with $\nu \doteq 10^{21}$, as proposed by Perrin (*Ann. Phys.* xi. p. 5. 1919). This would make a radioactive change essentially a photochemical process as distinct from a thermal process considered above. (For a discussion of this distinction, *cf.* Lewis and McKeown, *loc. cit.*) It can, of course, be argued that since radioactive changes are never instantaneous but obey the unimolecular law some preliminary species of activation is necessary, whether this be dependent on the action of radiation in the Perrin sense, or merely on some fortuitous spatial orientation (independent of temperature) in the nucleus which decomposes.

Summary.

Applying Einstein's concept of the mutual action of radiation and matter, and making use of a postulate in

this connexion advanced by Christiansen, the following expression has been obtained for the velocity constant of a unimolecular chemical change :—

$$k_1 = \frac{l^{b_m}}{p_n} \, . \, \nu \, . \, e^{-h\nu/kT}.$$

This agrees formally with the empirical equation

$$k_1 = \nu \, . \, e^{-h\nu . kT}$$

proposed by Dushman, and which has been shown by him to be in agreement with existing experimental data.

Department of Physical Chemistry,
University of Liverpool.

XXXII. *Note on the Velocity of a Unimolecular Chemical Reaction.* By W. C. M. LEWIS [*].

ON the basis of the expression employed by Planck for the rate of absorption of radiant energy by an oscillator, the act of absorption being regarded as continuous, the author pointed out more than three years ago (Phil. Mag. [6] xxxix. p. 26, 1920) that an expression for the velocity constant of a unimolecular change could be obtained which involved, amongst other quantities, a refractive index term.

If the refractive index term is identified with that of a gaseous system as a whole, its value is practically unity. On this basis the expression for the velocity constant was found to lead to a value which was only one ten-millionth of that actually observed. Lewis and McKeown (Journ. Amer. Chem. Soc. xliii. p. 1288, 1921) attempted to account for this discrepancy by assuming a greatly increased value for the actual refractive index of the individual molecules, in semi-quantitative agreement with an earlier conclusion of Lamb regarding the dielectric constant of a molecule (Trans. Camb. Phil. Soc. xviii. p. 348, 1900).

It was felt, however, that to account for the discrepancy on the basis of the refractive index *within* the molecule was physically far from satisfactory. The experimental facts lead one to the conclusion—provided absorption of radiation is the physical cause of chemical change— that Planck's expression for the rate of absorption by an

oscillator gives a value which is far too low, unless we can assume *either* that the radiation density exhibits fluctuations and is locally condensed close to and around the individual molecules of every material substance, *or* that the oscillator is capable of drawing upon the radiation present in a volume which is great compared with the magnitude which might be attributed to the oscillator itself *.

The latter possibility is attractive in view of a result obtained by the late Lord Rayleigh (Phil. Mag. xxxii. p. 188, 1916) on the rate of absorption by a *symmetrical* oscillator. It is doubtful whether it is legitimate to use this type of oscillator in the present case. Assuming that it is justifiable, we can make use of Lord Rayleigh's conclusion—namely, that such an oscillator in a given time will absorb the energy which passes through an area comparable with λ^2/π, where λ is the wave-length of the radiation concerned in the chemical change. This would mean that in one second the amount of radiation absorbed is that which would be present in a volume $\dfrac{\lambda^2}{\pi} \cdot \dfrac{c}{n}$, where c is the velocity of light *in vacuo* and n the average refractive index of the system for this wave-length. The radiation density being $u_\nu d\nu$, the amount of energy absorbed by such an oscillator per second is given by

$$\frac{\lambda^2}{\pi} \cdot \frac{c}{n} \cdot u_\nu d\nu,$$

which becomes

$$8h\nu \cdot \frac{1}{e^{h\nu/kT}-1} \, d\nu.$$

(It will be observed that the refractive index term has vanished.) For frequencies in the short infra-red, visible, and ultra-violet (which includes the chemically significant region), the expression becomes

$$8h\nu \cdot e^{-h\nu/kT} d\nu.$$

Dividing this by $h\nu$, we obtain the number of molecules each of which absorbs one quantum of the frequency ν during one second, and consequently we obtain for the unimolecular velocity constant the expression

$$k_{\mathrm{uni}} = 8e^{-h\nu/kT} d\nu, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $d\nu$ represents the width of the band or range of

---

* In the long run these two possibilities may not be very different.

frequencies which the molecule is capable of absorbing round about frequency ν.

The width of a band is usually defined as that spectral region over which the absorption coefficient falls to one-half of the maximum value which it possesses at the head or optical centre of the band (Ribaud, *Annales de Physique*, xii. p. 188, 1919). Ribaud (*Comptes Rend.* clxxi. p. 1134, 1920) considers that the width of a band (as distinct from that of a line) is defined solely by the position of the head of the band at which absorption occurs. Thus for band heads at $270\ \mu\mu$, $500\ \mu\mu$, and $3\cdot3\ \mu$ Ribaud finds the corresponding widths to be $42\ \mu\mu$, $77\ \mu\mu$, and $720\ \mu\mu$ respectively. As a first approximation, therefore, we can write $\lambda = 6\,d\lambda$ or $d\nu = 0\cdot17\nu$. Equation (1) would then take the form

$$k_{\text{uni}} = 8 \times 0\cdot17\nu \cdot e^{-h\nu\,k\text{T}}. \quad . \quad . \quad . \quad . \quad (2)$$

Owing to the approximate nature of the initial assumption —namely, that the oscillator absorbs the energy which passes through an area comparable with λ^2/π,—it follows that no precision can be attributed to the numerical term $(8 \times 0\cdot17)$. It would appear, however, that the expression (2) is capable of giving values comparable with those given by the empirical equation of Dushman, namely $k = \nu \cdot e^{-h\nu\,k\text{T}}$, which, for the case of gaseous systems and for dissolved gases, has been found to accord fairly well with the experimental values, although it should be pointed out that very considerable discrepancies are found in the cases in which a *non-volatile* solute decomposes in solution in a unimolecular manner.

Department of Physical Chemistry,
University of Liverpool.

XXXIII. *Note on the Chemical Constants of Diatomic Gases. By* J. R. PARTINGTON, *D.Sc.*[*]

IN the Philosophical Magazine for November 1922 (vol. xliv. p. 988) I obtained an expression for the chemical constant of a diatomic gas which (equation 15 in the paper) is

$$\log_e \frac{m^{5,2}\,r^2\,2^{7/2}\,\pi^{7,2}\,k^{7/2}}{h^5} \quad . \quad . \quad . \quad . \quad (1)$$

or $\qquad C = 12\cdot730 + 2\cdot5\log M + 2\log r$

for the case of a molecule composed of two like atoms.

I now find that an expression reducing to the above had been found by the late Dr. Sackur by a slightly different method. In a paper in the *Annalen der Physik*, vol. xl. p. 98 (1913), he gives an expression which, when applied to the case considered, reduces to

$$C = 12\!\cdot\!548 + 2\!\cdot\!5 \log M + 2 \log r$$

and on p. 95 he obtains an expression (when the atoms are identical),

$$\log_e \frac{m^{5\cdot 2}\, r^2\, 2^{9\cdot 2}\, \pi^{7\cdot 2}\, k^{7\cdot 2}}{h^5},$$

which differs only by the addition of $\log_e 2$ from (1), since the case investigated by Dr. Sackur was that mentioned on p. 993 of my paper, where it is stated that $\log_e 2$ must be added. (Slightly different values for k and h were used by Dr. Sackur.)

I am still of the opinion that for a molecule composed of two identical atoms, the expression given by Dr. Sackur is in excess of the correct value by $\log_e 2$.

In my paper I also referred to the possibility of quantizing the angular momentum instead of the rotational energy ; the latter would follow from the considerations advanced by Bjerrum[*] : it is a very simple matter to modify the calculation, taking the expression $\nu = nh / 4\pi^2 \mathrm{l}$ instead of $\nu = nh / 2\pi^2 \mathrm{I}$.

XXXIV. *On the Mechanism of the Electric Arc.*

To the Editors of the Philosophical Magazine.

DEAR SIRS,—

WITH reference to a recent contribution on the electric arc by Professor Duffield (June 1923) I am sorry to find that he and I are still in disagreement in the interpretation of the results he obtained. He criticises my use of deductions on the ionic distribution in the body of arc in the discussion of what takes place very near to the cathode. This criticism would be justifiable if we were concerned in his theory only with the repulsion of the cathode. But he explains the repulsion of the anode by postulating that electrons are projected from the cathode and communicate their momentum to the anode. Mr. Beer and I searched for them directly

[*] *Ber. Deutsch. Phys. Ges.* xvi. p. 640 (1914).

and indirectly in the intervening space, the body of the arc which they would have to cross, and failed to find them there. I feel, therefore, that the failure of this test is a serious objection to his theory.

With regard to my suggested explanation of the repulsion of the poles I am afraid that I cannot have made my argument quite clear. Except close to the electrodes an ion travels with an average velocity determined by the field and the frictional drag of the ion on the gas. We are agreed that the resultant effect on the electrodes of this process is nil. But in the initial stage of its motion an ion starting from rest at the electrode surface must accelerate in order to acquire this average speed—in other words it is acquiring more momentum than it is imparting to the gas. I still maintain therefore that the electrode must feel the reaction whether the ion reaches its final average velocity rapidly or slowly. And whether an assumption such as I suggested, namely that the negative ions are charged atoms (which leads to a quantitative agreement with experiment) is justified or not, a reaction of some magnitude must be there.

Professor Duffield appears in one case to dislike my terminology. I do not quite see his reason for doing so. When ions moving from an electrode through a gas at atmospheric pressure exert a drag upon the gas they tend to set up behind them a region of lower pressure into which other gas or the electrode itself, if free, will move. I feel myself that the term 'suction' is a convenient and brief term for expressing this process.

I am,
Yours faithfully,
A. M. TYNDALL.

University of Bristol.
June 11th, 1923.

XXXV. *The Octet Theory of Induced Alternate Polarities : the Domains occupied by Octet-stable and Octet-unstable Centres.* By RONALD FRASER *and* J. E. HUMPHRIES, *B.A., M.Sc., Chemistry Department, University of Aberdeen*.*

THE authors have recently (Chemical News, 1923, cxxvi. pp. 241, 257) applied the Lewis-Langmuir theory of covalence to the elucidation of the principles underlying numerous groups of facts and empirical rules in organic chemistry. The discussion rests primarily on an electronic

* Communicated by Prof. A. Findlay, M.A., D.Sc.

interpretation of Lapworth's Principle of Induced Alternate
Polarities, similar to that advanced by Kermack and Robin-
son (Jour. Chem. Soc. 1922, cxxi. p. 427). We differ from
these authors, however, in postulating an electron trans-
ference as between stable and unstable octets as a necessary
accompaniment of the manifestation of induced alternate
polarity ; that this is not their view was made clear by
Professor Robinson at the Hull Meeting of the British
Association, 1922. There appears to us to exist a certain
amount of justification for our assumption : it is now widely
recognized that there is no essential distinction between polar
and non-polar compounds (G. N. Lewis, Jour. Am. Chem.
Soc., 1916, xxxviii. p. 762 : Briggs, Jour. Chem. Soc., 1921,
cxix. p. 1879 ; Kermack and Robinson, *loc. cit.*: Stieglitz,
Jour. Am. Chem. Soc., 1922, xliv. p. 1293) ; in an extreme
case of the attainment of octet stability, such as that of the
chlorine ion in the strongly polar compound NaCl, there is
no doubt that electron transference has taken place ; and it
seems only in accordance with continuity to suppose that a
chlorine atom in, say, monochlorbenzene has drawn an
electron to itself from the carbon atom to which it is attached.

Further, in the extreme case of octet stability where the
octet can exist free as an ion, its reactivity is exceedingly
great; and we have found, in an examination of numbers of
organic compounds in the light of the octet theory, that
reactivity and octet stability run parallel. Perhaps it would
be carrying the argument too far to assume ionization,
even momentary, in such cases ; but in any event it would
appear that the more nearly a substituent approaches octet
stability, the more it should spread from the nucleus.   In
view of the impossibility at present of determining the
relative sizes of stable and unstable octets, we have been led
by the above reasoning to seek a vindication of our opinion
by considering the domains occupied by stable and unstable
centres attached to the benzene nucleus.

Possible methods of attack include : (*a*) *Viscosity measure-
ments*. An application to the present problem is immediately
suggested of the methods employed by A. O. Rankine to
determine the sizes of the protuberances formed by hydrogen
atoms on molecules containing hydrogen (Rankine, Proc.
Far. Soc., 1922, xvii. Part iii.). Unfortunately, the benzene
derivatives we should wish to examine are liquids or crystal-
line solids, and an examination of these in the gaseous state,
as would be demanded by Rankine's methods, presents con-
siderable experimental difficulties : (*b*) *Critical data*. It has
been pointed out by Chapman (Phil. Trans. Roy. Soc., 1916,

ccxvi. p. 279), that molecular sizes deduced from viscosity measurements and from the b_c of van der Waals' equation are in excellent agreement, for molecules containing up to three atoms. The bodies we should wish to examine contain six or more atoms, so that in such case too much faith could not be placed in the agreement noted by Chapman. There seems little doubt, however, that the foregoing are the best methods available; as has, indeed, been remarked by Wöhlisch (Z. Elektrochem., 1921, xxvii. p. 295).

Owing to the time which must necessarily elapse before the results of extended inquiry along these lines may be available, we venture to think that the interest of the point at issue warrants our presenting here certain data which appear to lend support to our view, namely, that electron transference as between stable and unstable octets accompanies the manifestation of induced alternate polarity. We have made a re-examination of the work of Jungfleisch (Compt. Rend. 1867, lxiv. p. 911), and Le Bas (Phil. Mag. 1914, xxvii. p. 988), on the molecular volumes of various chlorbenzenes; we have taken merely the average volume of the chlorine atoms in each several compound, as we feel that the additive principle of Kopp can be pushed too far in investigations of this kind. Below are placed the ideographic representations of the compounds, with the state of octet stability and instability of the chlorine atoms indicated by $-$ and $+$ respectively. The figure beneath each compound is the average volume of the chlorine atoms, as computed

Fig. 1.
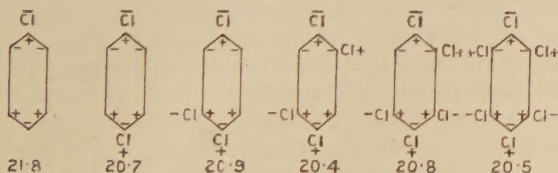
from the data of the authors mentioned. It will be seen that, in every case, the introduction of an octet-stable ($-$) chlorine causes an increase in the average volume of the chlorine atom, that of an octet unstable ($+$) chlorine a decrease, just as one would be led to expect on our view.

There is a further result of considerable interest; it might, in fact, be regarded as something in the nature of a crucial test. It will be observed that in all the compounds examined by Jungfleisch, certain of the chlorine octets are

stable, others unstable. Now, in the case of *m*-dichlor-
benzene, we regard *both* chlorine atoms as in a state of
octet stability ; they are, therefore, reinforcing each other's
tendency to spread from the nucleus ; and hence, if our
reasoning is correct, the average volume of the chlorine
atoms in this compound should be greater than in any of the
former cases where no such reinforcing effects existed. We
have calculated the molecular volume of *m*-dichlorbenzene
at the boiling-point (172°C.) from its density at 0°C. (1·307 ;
Beilstein, vol. ii. p. 44) by means of the formula due to Le
Bas (Proc. Chem. Soc., 1914, xxx. p. 86) :

$$d_0/d_t = 1 + c\left(1 - \frac{273}{\text{B. P.}}\right), \text{ where } c = 0\cdot46.$$

The following figure gives the state of polarity of the
constituent atoms of *m*-dichlorbenzene, and the average
volume of the chlorine atoms, which may be taken to be
correct to within 1 per cent. (Le Bas, *loc. cit.*). It should
be compared with the first group.

Fig. 2.

21·5

The result is in accordance with prediction, the average
volume of the chlorine atoms being about 3 per cent. greater
than the largest value (20·9) obtaining in the polysubstituted
members of the former group. (Monochlorbenzene appears
to stand apart from the general run of the results.) *

We consider the above data to give at least a pointer
towards the correctness of our ideas, and, as such, to be of
some interest ; but it would be unwise to make any general
statement at the present stage, until more extended results
may be available for discussion.

We are glad of this opportunity of expressing our gratitude
to Professor Alex. Findlay for his interest and constant
encouragement.

* Fry ('The Electronic Conception of Valence and the Constitution
of Benzene,' 1921, p. 177 seq.) has advanced a different interpretation of
the results of Jungfleisch ; but his theory leads to many inconsistencies,
and it does not seem possible to predict, on the basis of his conceptions,
the decided increase in the average volume of the chlorine atoms in
m-dichlorbenzene.

XXXVI. *A New Phenomenon**. *By* MARSHALL HOLMES.

THE phenomenon to be described in this paper is thought to be new, and although it has a direct bearing on a larger question now being investigated, it is perhaps sufficiently interesting to warrant publication by itself.

The apparatus used was arranged in the manner shown:—
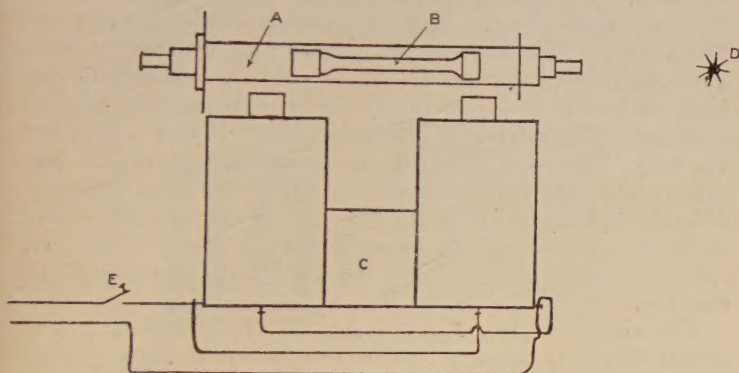
A is a polarimeter ; B is the polarimeter cell containing a substance suitable for the investigation; C is an electromagnet with the bobbins arranged across the bed; D is the source of light; and E is the switch. The nicols are arranged so that the polarimeter field appears uniform at first.

To obtain the phenomenon, the polarimeter cell is filled with a suitable liquid—glycerine was generally chosen— and placed in position in the polarimeter. The polarimeter field still appears uniform as glycerine is optically inactive. The current through the magnet is now switched on and the magnetic rotation produced causes part of the field to appear dark. If the adjustment of the polarimeter is left unaltered, and the current is now switched off again, attention being meanwhile steadily directed on the image, it will be seen that it first fades rapidly away and then just reappears with the light and dark parts reversed before the field finally becomes quite uniform, so that if the magnetic rotation has originally been *dextro* the reversed rotation is *lævo*, or if it has been *lævo* the change is to *dextro*. What happens with most substances is that the field becomes quite uniform immediately the current is switched off, and it remains uniform. With glycerine, however, such is not the case.

The phenomenon takes place and disappears very quickly,

* Communicated by the Author.

the average period elapsing from the time the current is interrupted till the field appears uniform being only a second or a second and a half long. The amount of reverse rotation is also very small ; it has never been found to be more than one degree of arc, and consequently it is rather difficult to observe. That there is a real rotation is shown, however, by the fact that it appears with only a very few liquids ; if the phenomenon were merely subjective it would be expected with all liquids. Those that showed it were glycerine, and solutions of citric acid in glycerine, and apparently also an aqueous solution of lead acetate slightly acidified with acetic acid. Liquids with a low or a very low viscosity did not exhibit the phenomenon ; glycerine, and certain solutions in glycerine with about the same viscosity, did exhibit it ; and still more viscous substances again failed to show any reversal, although one or two of the last appeared to show a slight lag in losing their magnetic rotation.

The simplest explanation seems to be furnished by the assumption that *magnetic molecules* exist in the liquid just as they are supposed to exist in a bar of iron, and that owing to the high viscosity each of these molecules has only a limited freedom of movement, that it has a position of meta-stable equilibrium ; consequently when the magnetic field is induced these molecules are placed in a state of strain, and when the stress is removed they swing past the positions of equilibrium and a rotation opposite to the magnetic rotation is shown. That the phenomenon does not occur when the viscosity is low may be due to either of two causes or to a combination of both ; possibly something does take place, but so quickly that the eye cannot follow the changes ; or more likely owing to the low viscosity of the liquid there is no position of equilibrium unless when the magnetic field is present. Another explanation is required for the absence of the reversal in liquids of a very high viscosity. In these cases a sufficient reason is probably furnished by the fact that the stresses due to the magnetic field are relatively small when compared with the stresses already existing in the liquid, so that when the magnetic field is removed only a comparatively insignificant change is made in the total of the forces present.

Before any hypothesis can be definitely accepted, however, much more work is yet to be done. All that is quite clear is that the phenomenon occurs.

The Sir Donald Currie Laboratories,
  Queen's University, Belfast.